

Subtractive Etching of Cu with Hydrogen-Based Plasmas

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Outline

- Introduction
- Two-step etch process at low temperature
- Hydrogen plasma etching of Cu
- Summary
- Acknowledgements



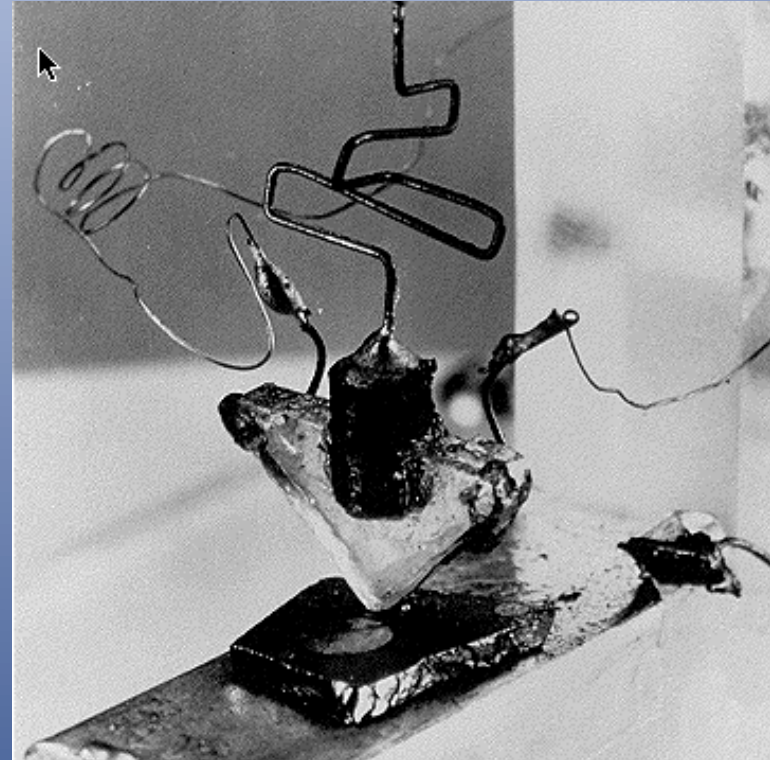
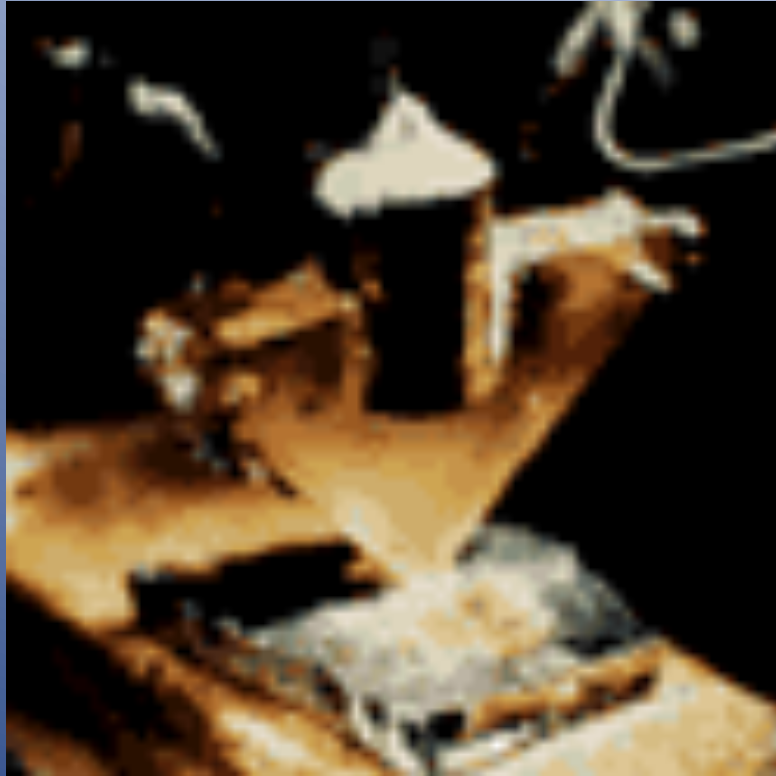




A Brief History of the Transistor

The First Transistor

Transistor = TRANSfer + resISTOR



John Bardeen and Walter Brattain at Bell Laboratories constructed the first solid-state transistor. This PNP point-contact germanium transistor operated with a power gain of 18 on Dec. 23, 1947. With their manager, William Shockley, they won the Nobel Prize in 1956.

The First Transistor Product

The first transistor radio was a joint project of the Regency Co. and Texas Instruments.



Sony

In Japan, a tiny company had other ideas. **Tsushin Kogyo** was close to manufacturing its first radios when it heard that an American company had beaten them to market. But they persevered and made a radio, the TR-52. When Regency quit producing their radio, the Japanese company immediately started shipping their radio to the U.S. One immediate problem was that Americans couldn't pronounce their name. The founders, Ibuka and Morita, thought of using a Latin word **sonus** ("sound.") Akio Morita knew some English, and made a simple variation that became their name from then on:

SONY

Jack Kilby's First Integrated Circuit

(An oscillator circuit on germanium substrate)

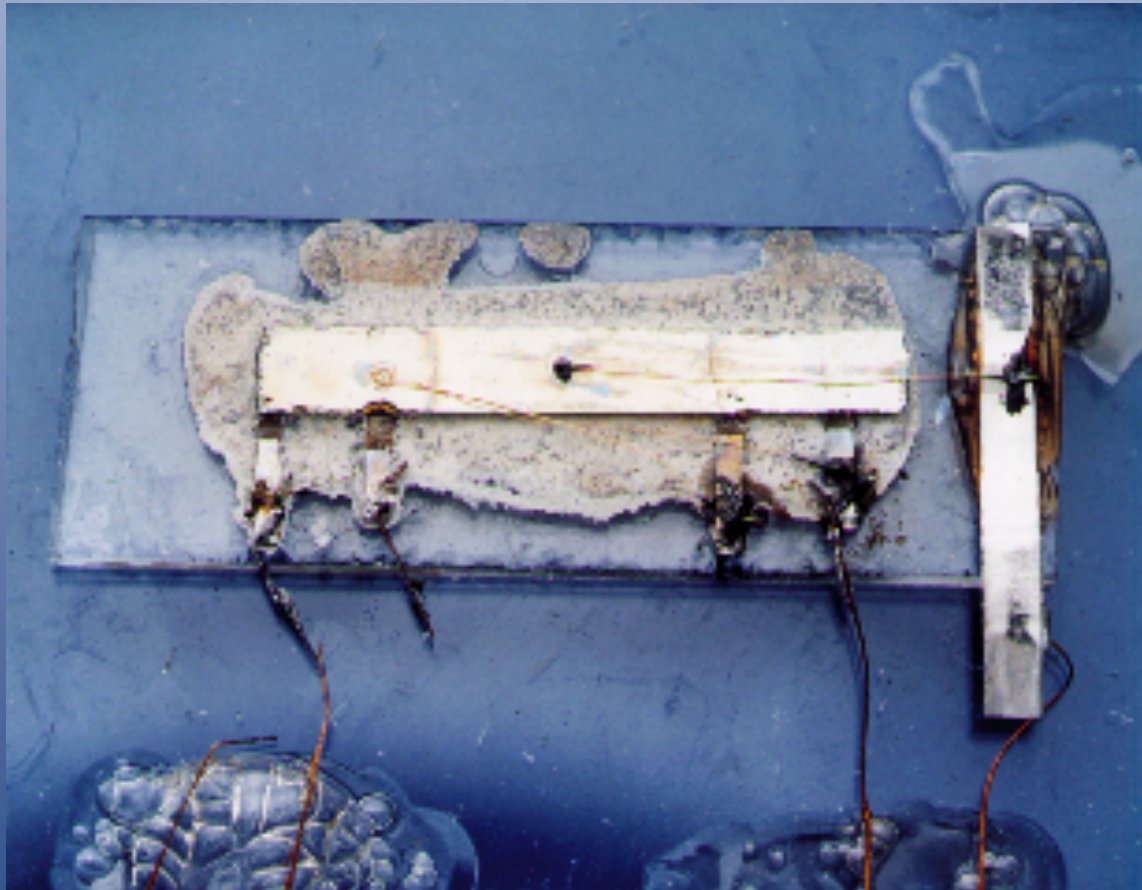
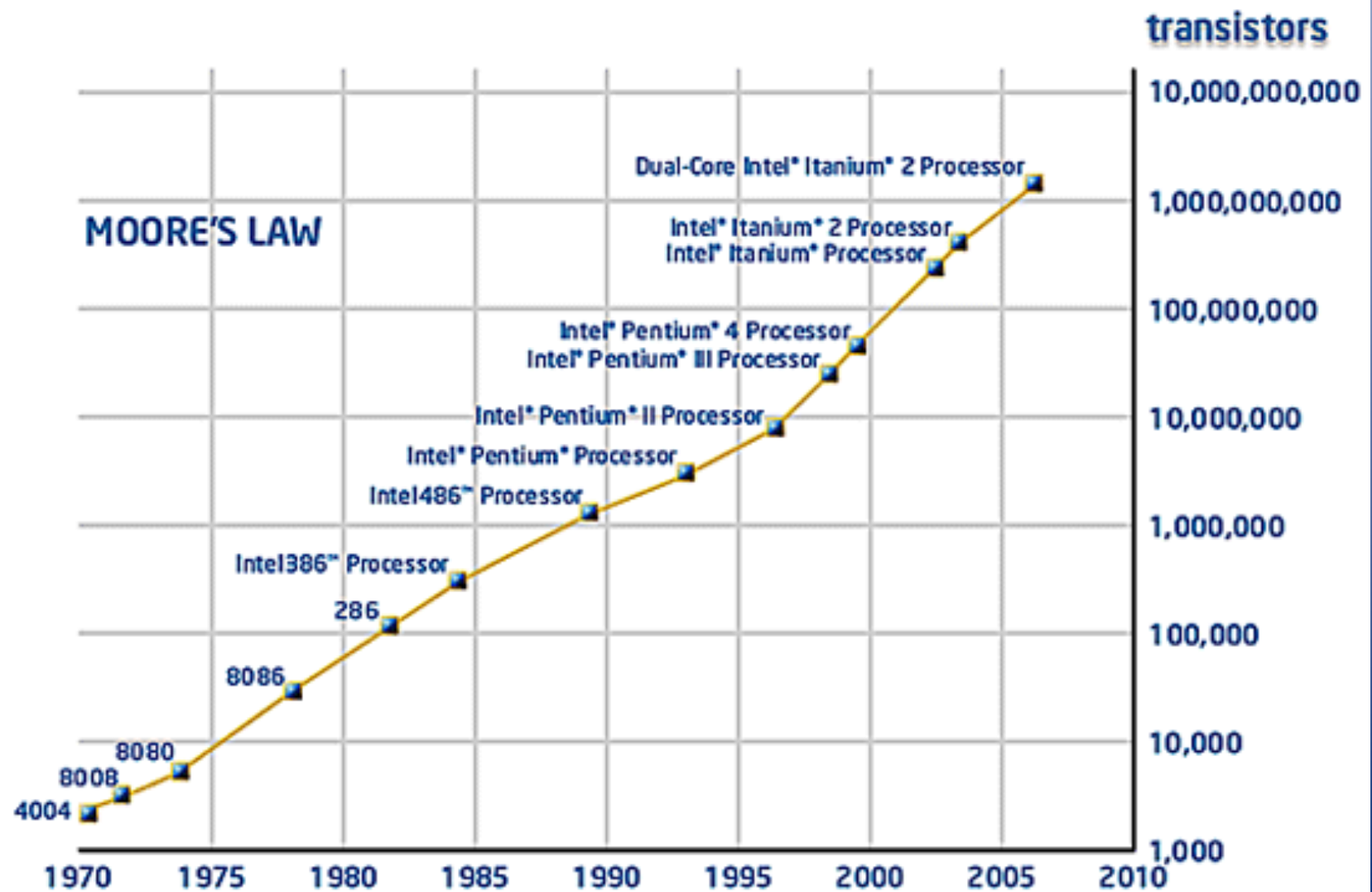
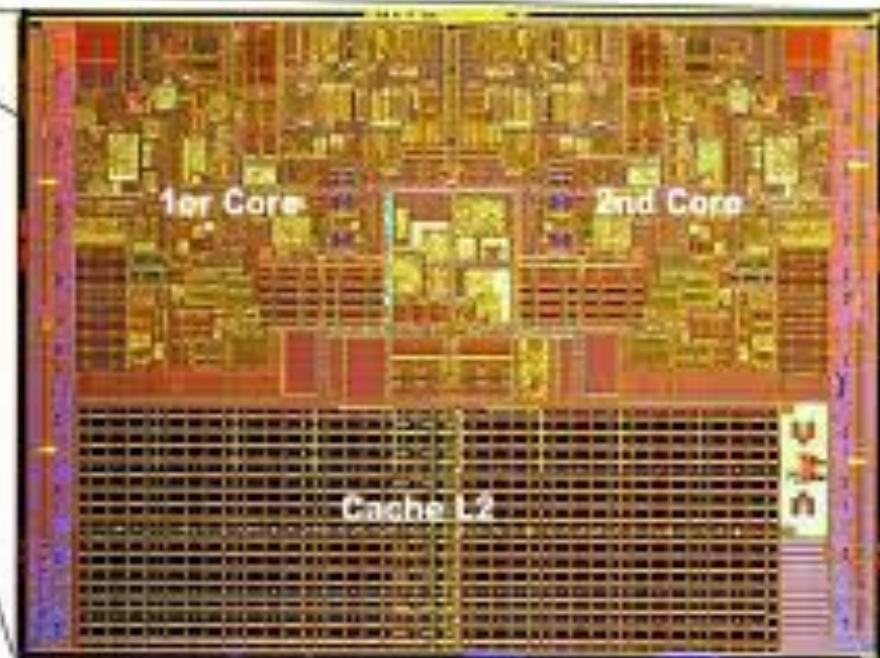
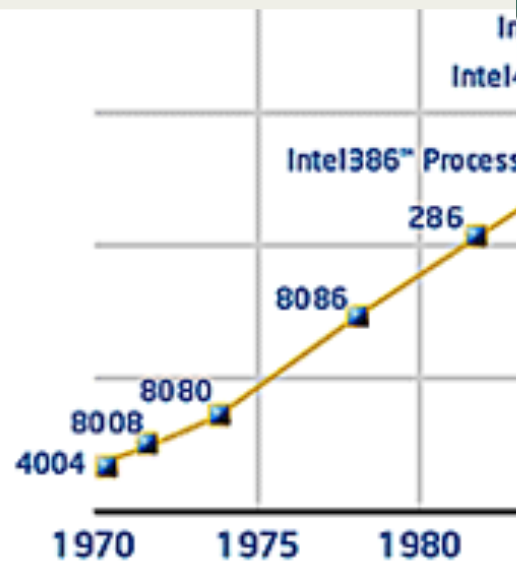
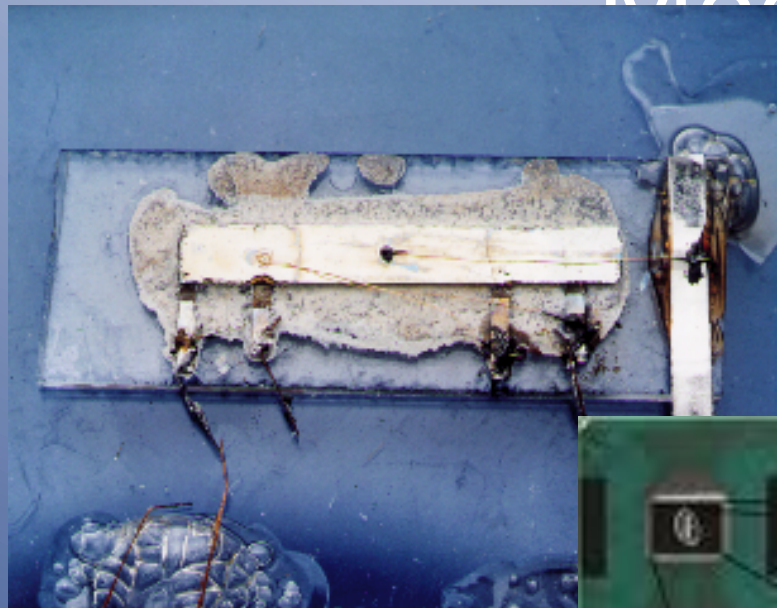


Photo courtesy of Texas Instruments, Inc.

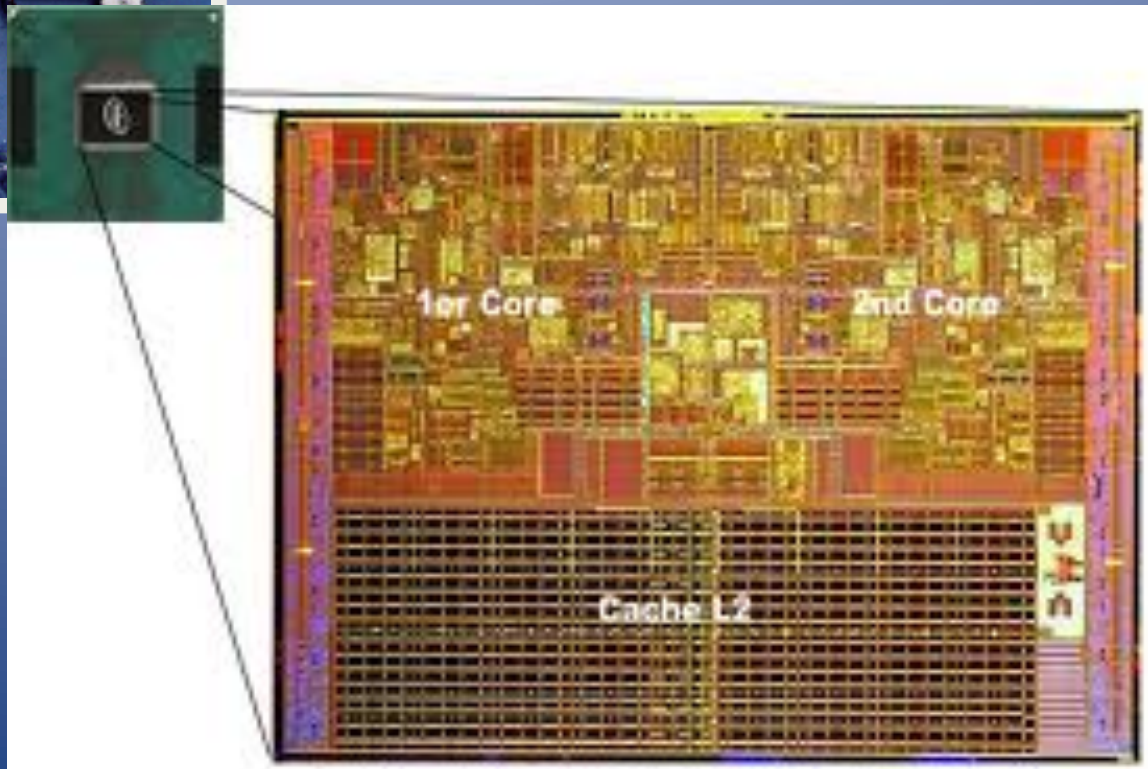
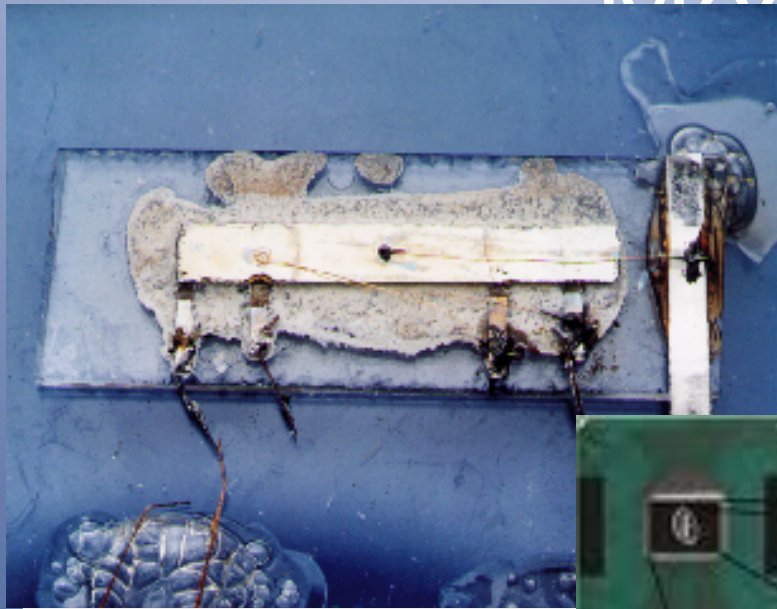
Moore's Law



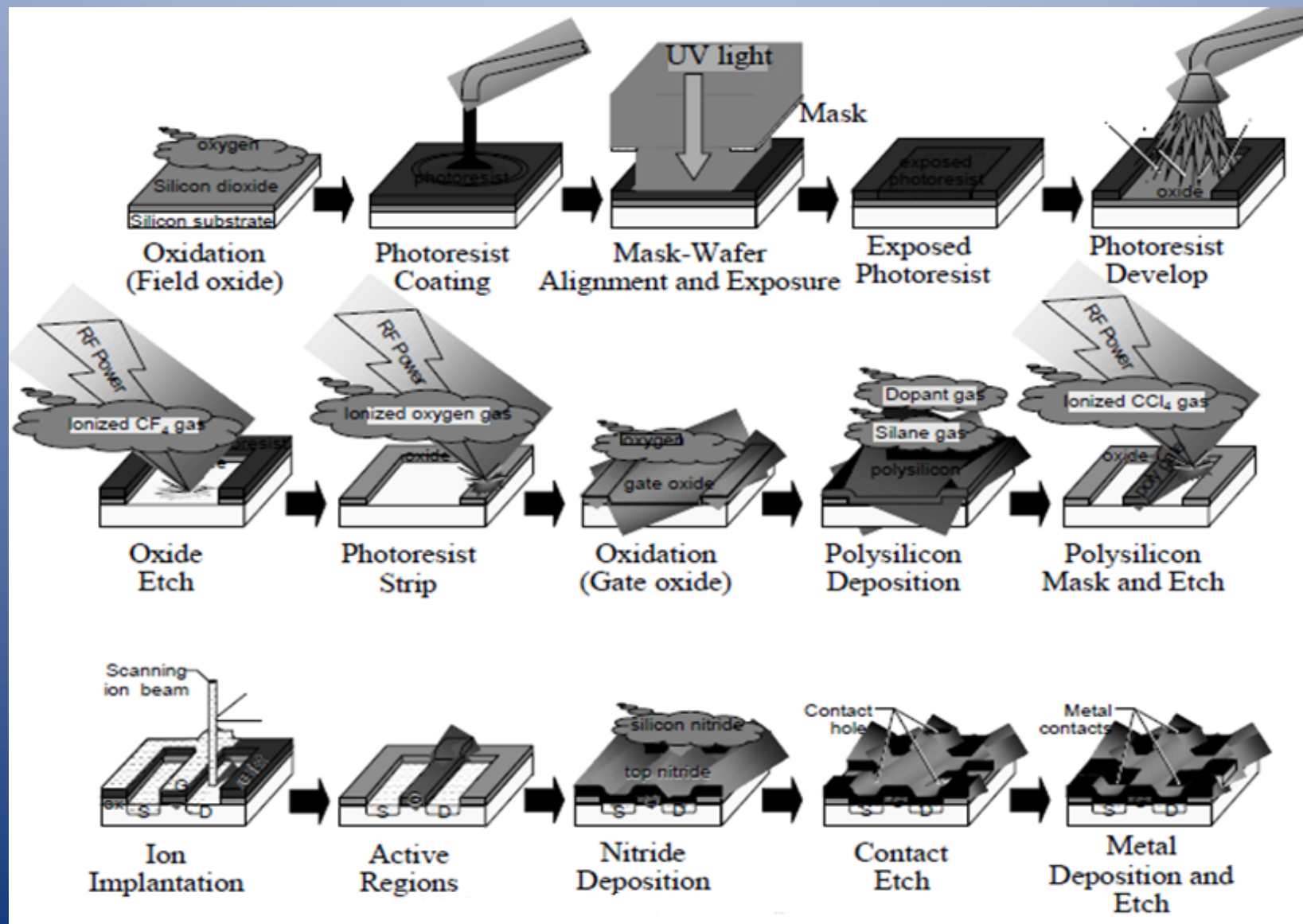
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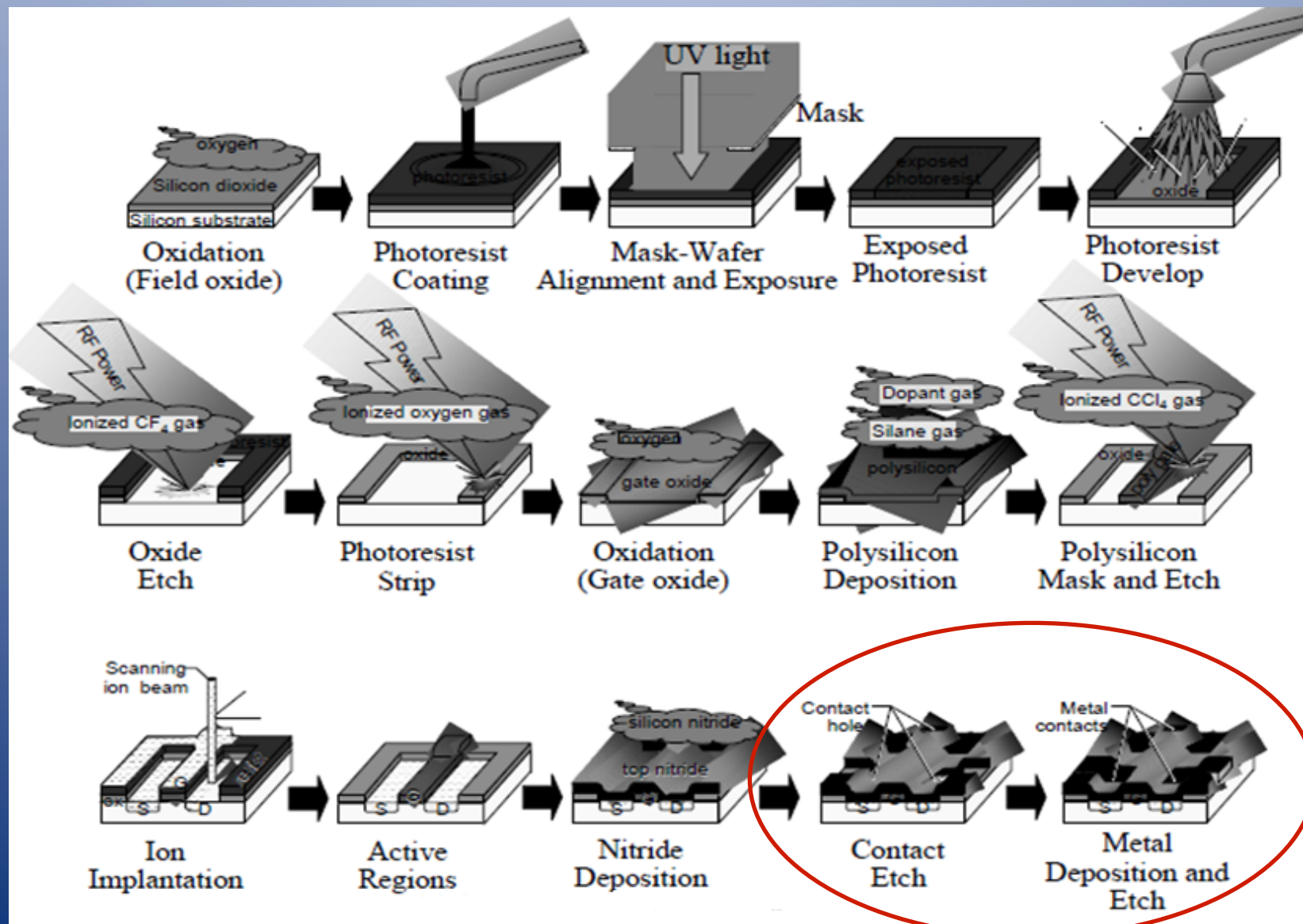


Major Fabrication Steps in MOS Process Flow



Adopted from Michael Quirk & Julian Serda © october 2001 by Prentice Hall

Major Fabrication Steps in MOS Process Flow



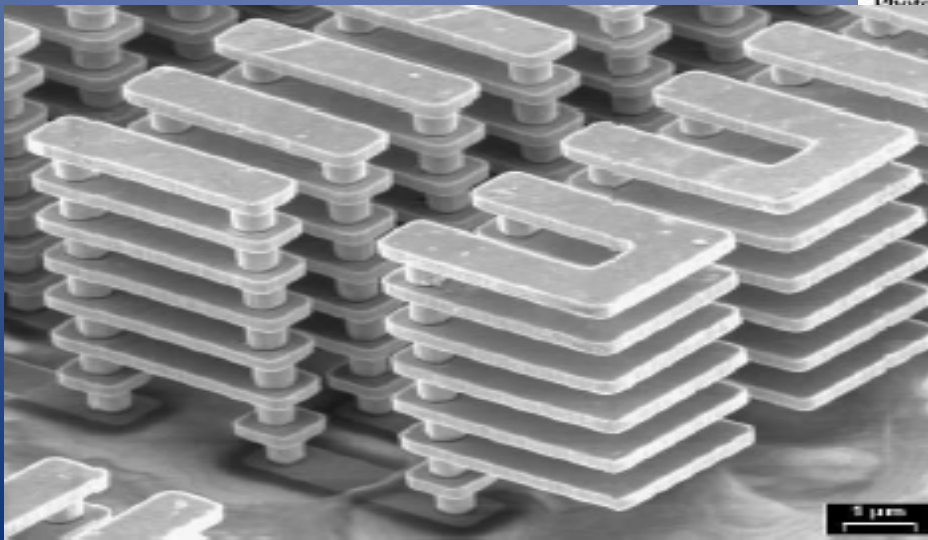
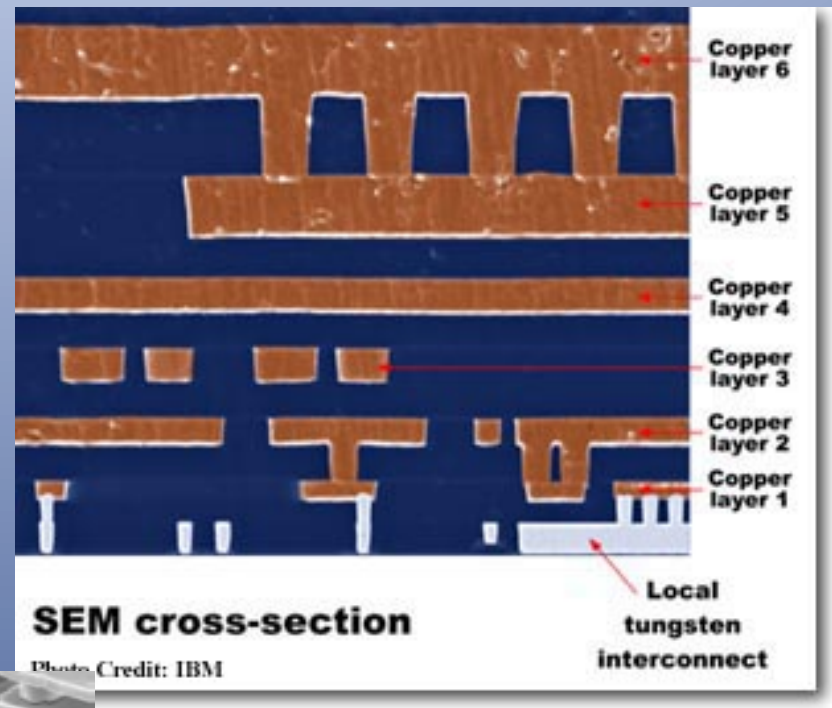
Adopted from Michael Quirk & Julian Serda © october 2001 by Prentice Hall

Metal interconnect

- Many layers of metal interconnect are possible.
 - 12 layers of metal are common.
- Lower layers have smaller features, higher layers have larger features.
- Can't directly go from a layer to any other layer.

Metal interconnect

www.chips.ibm.com

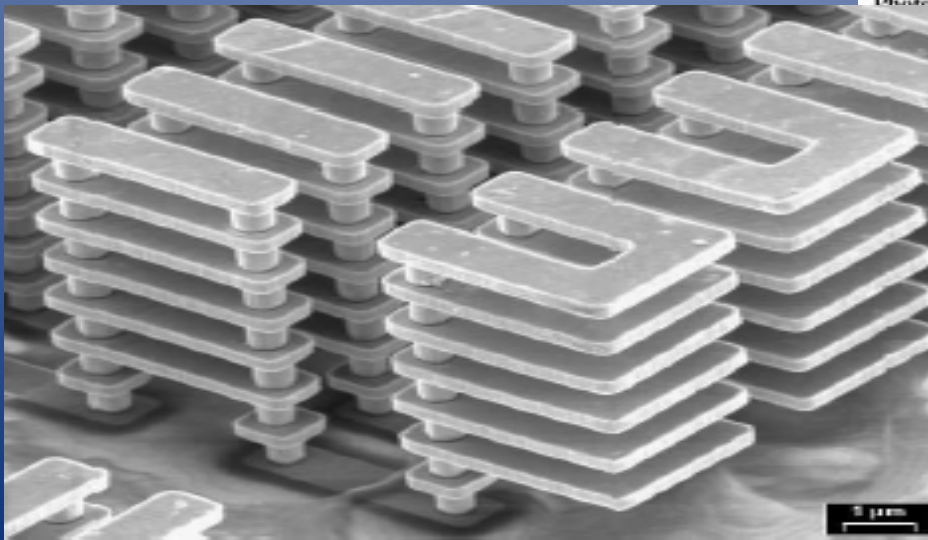
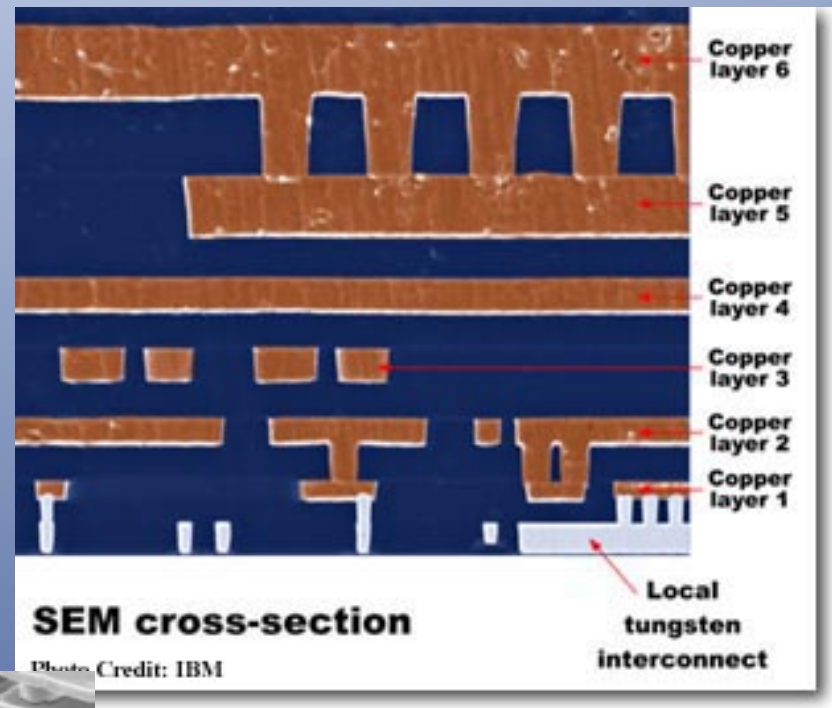


layers of copper interconnects
fabricated at IME, Singapore

Property of Interconnect Materials

Material	Thin film resistivity ($\mu\Omega - \text{cm}$)	Melting point ($^{\circ}\text{C}$)
Cu	1.7-2.0	1084
Al	2.7-3.0	660
W	8-15	3410
PtSi	28-35	1229
TiSi ₂	13-16	1540
WSi ₂	30-70	2165
CoSi ₂	15-20	1326
NiSi	14-20	992
TiN	50-150	~2950
Ti ₃₀ W ₇₀	75-200	~2200
polysilicon (heavily doped)	500-1000	1410

Metal interconnect

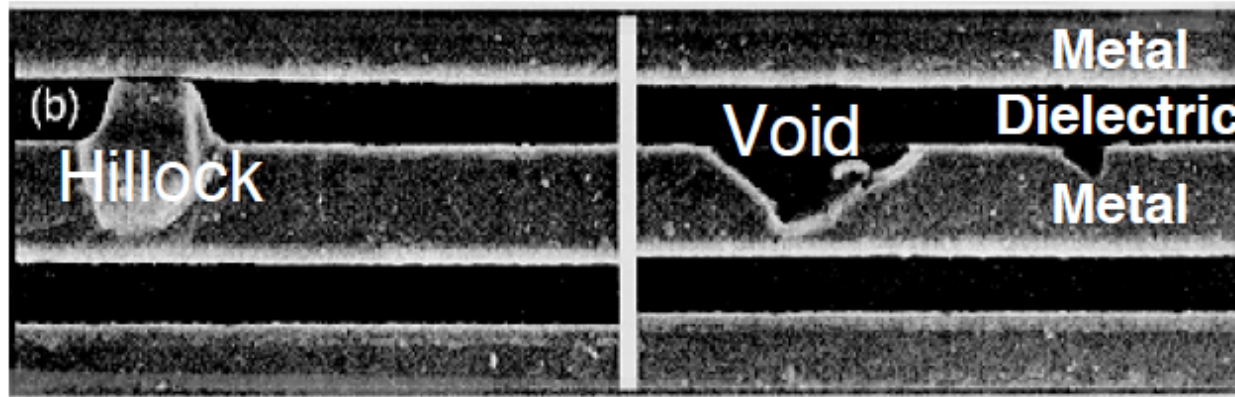


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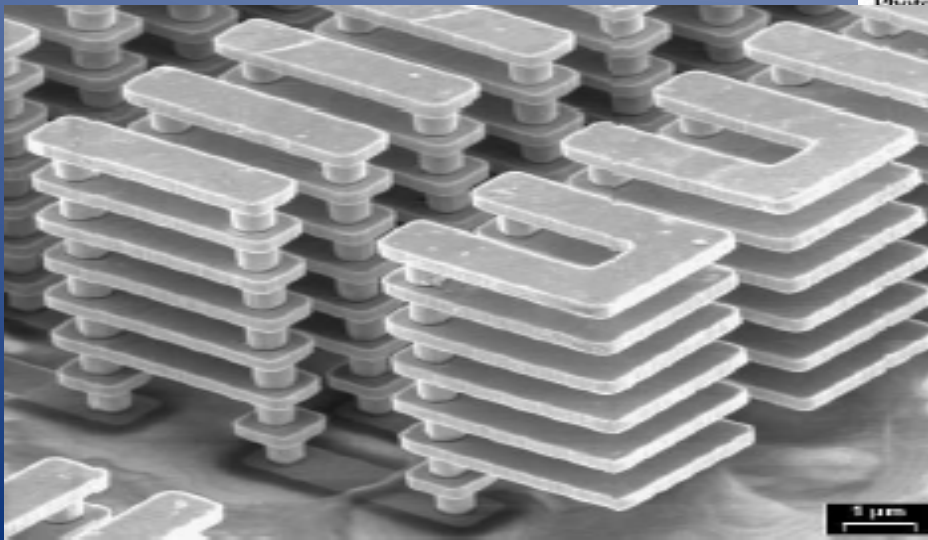
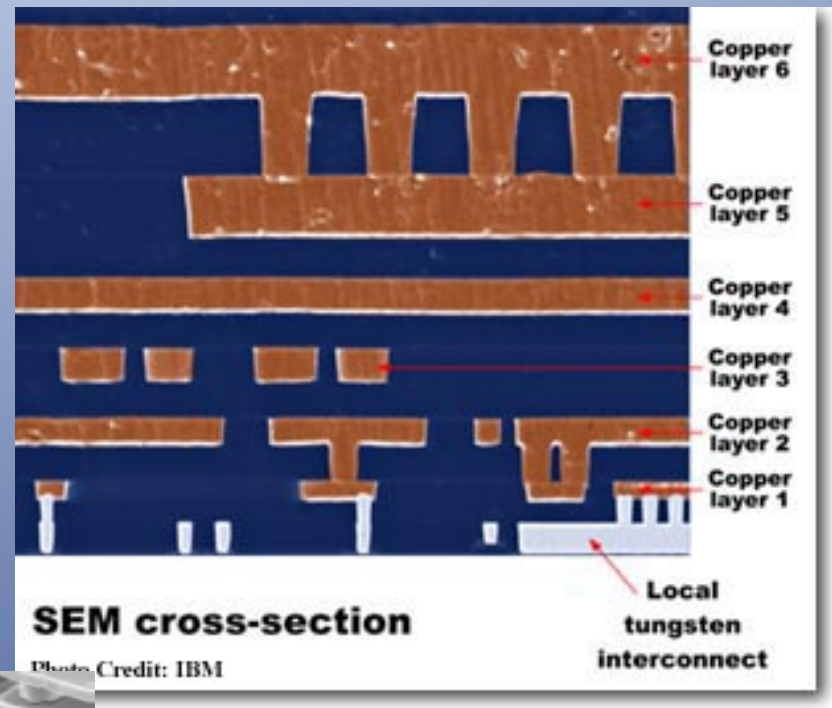
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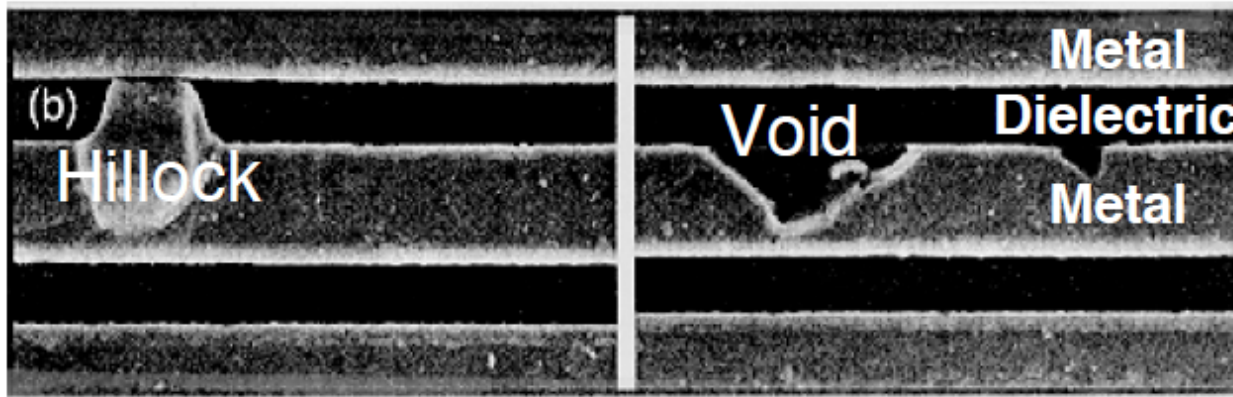


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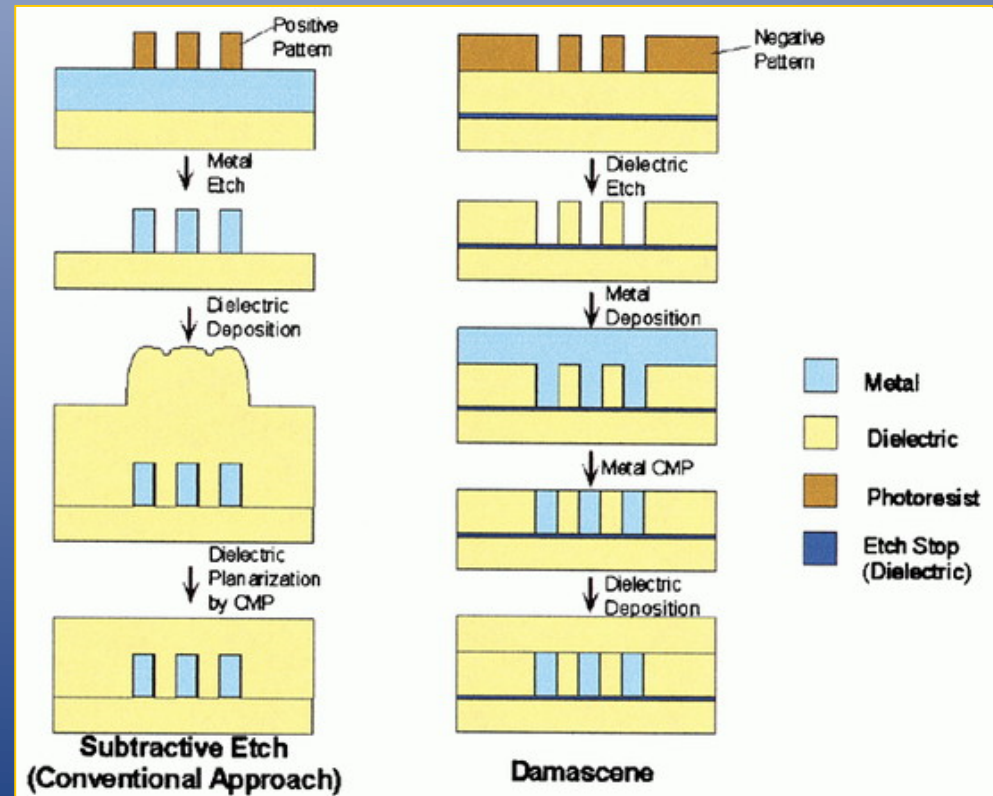
Copper Metallization & Damascene Technology

- An effective fully plasma-based subtractive etch process for Cu has not been developed primarily due to the inability to form volatile etch products for Cu etching at temperature $<200^{\circ}\text{C}$.

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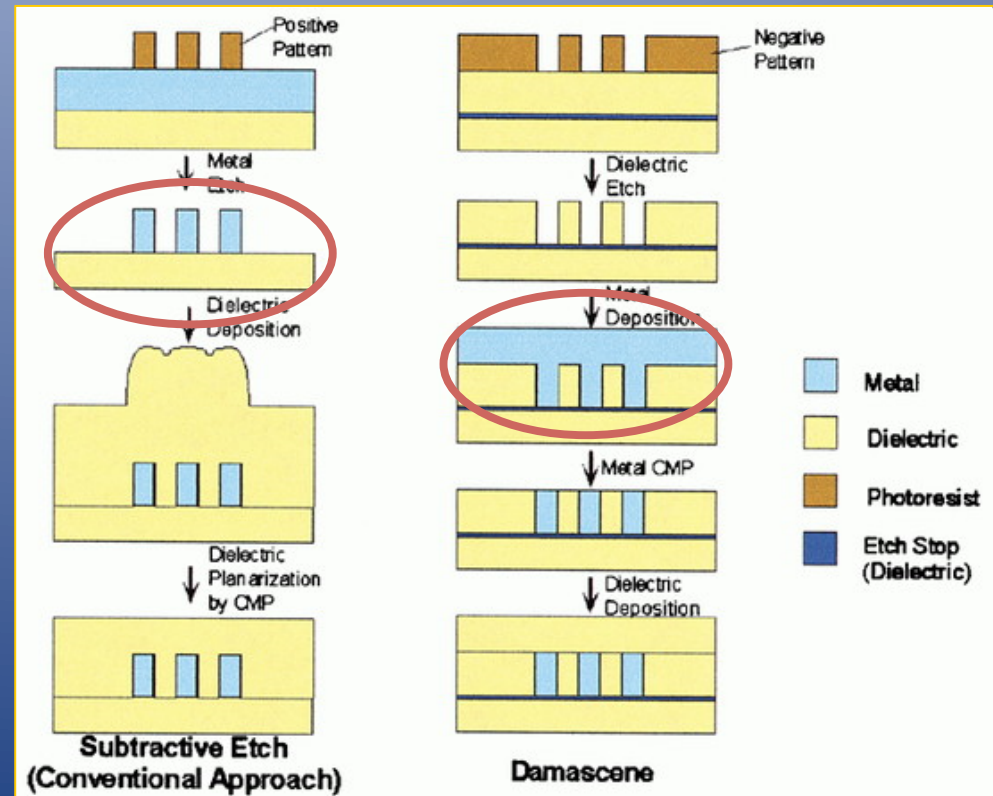
IBM introduced Damascene Technology in the mid 1990s.



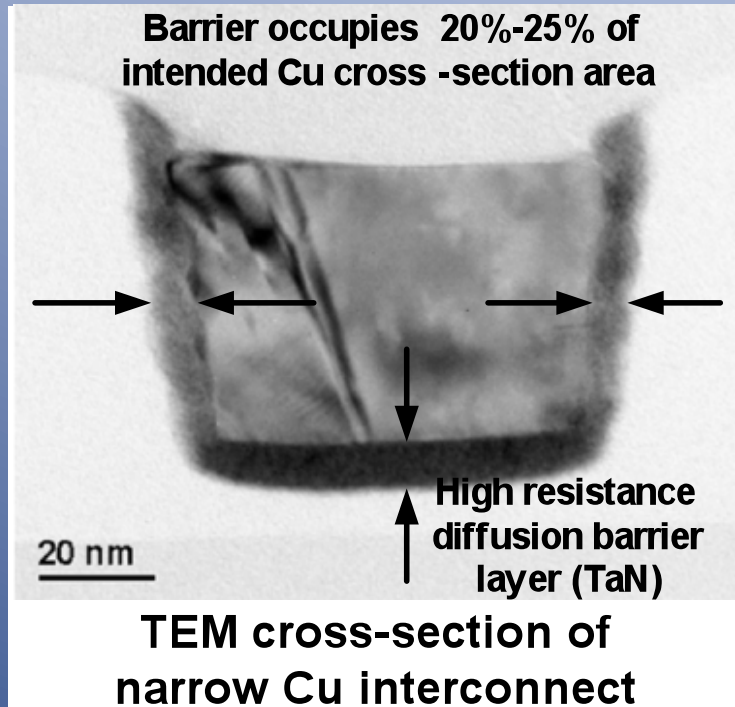
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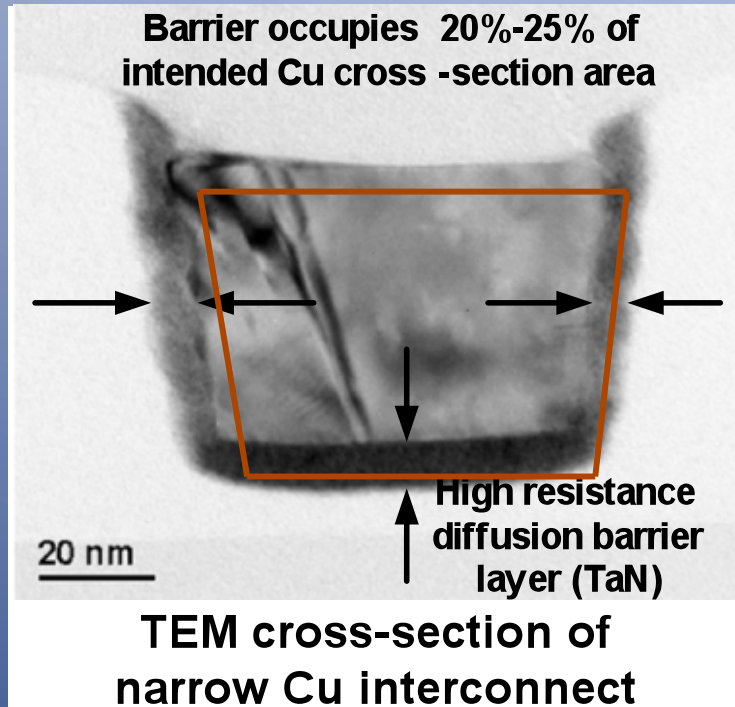
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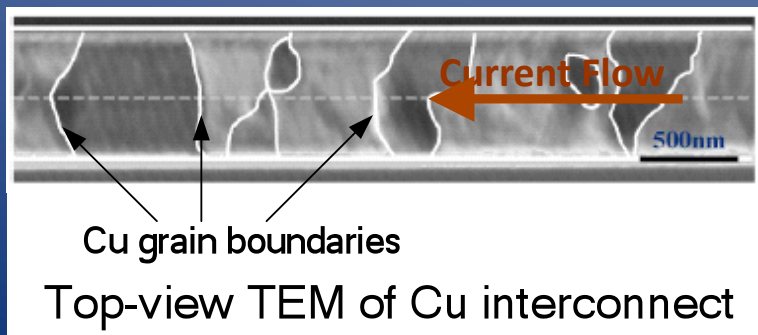
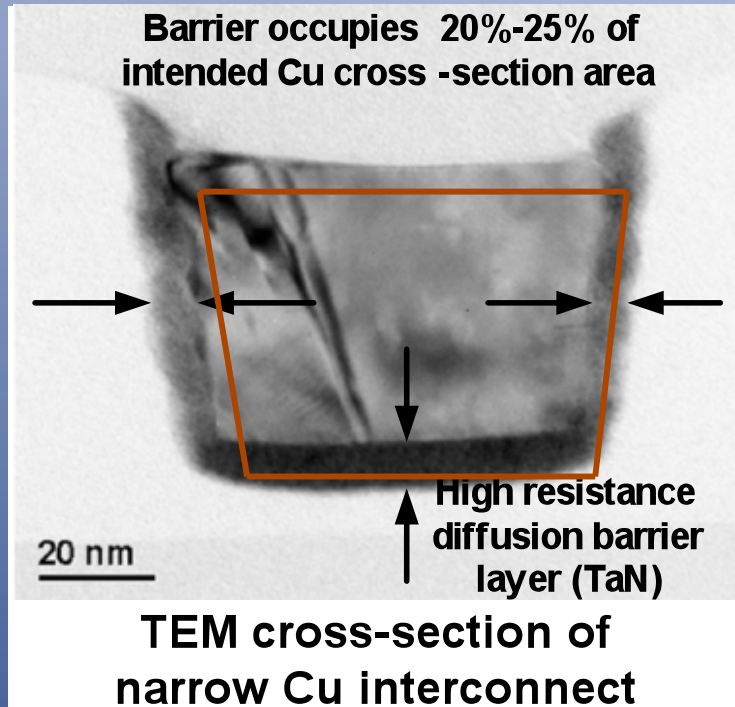
Cu Interconnect Resistivity Increase



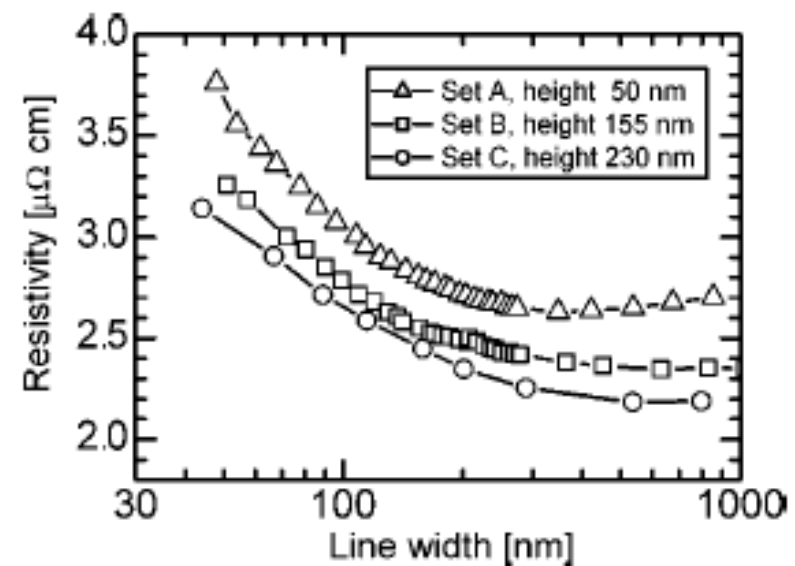
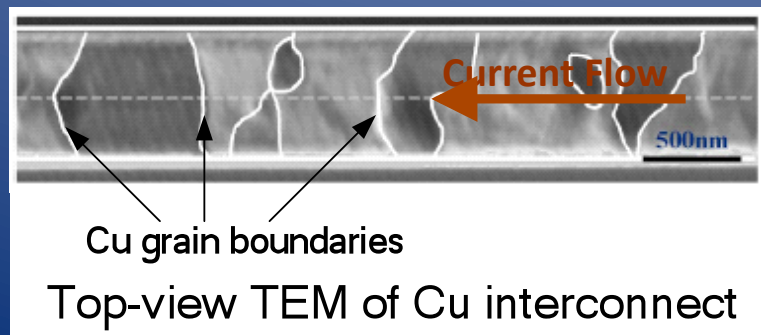
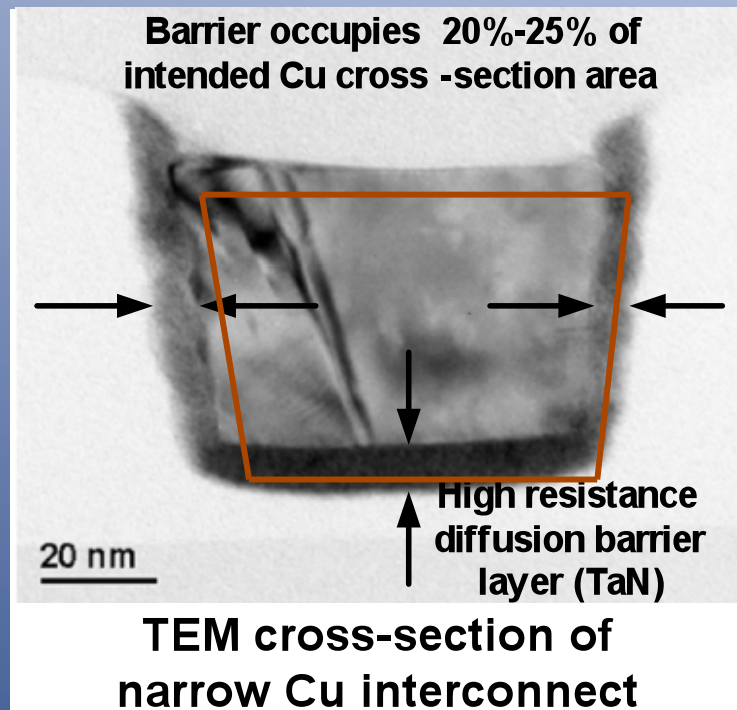
Cu Interconnect Resistivity Increase



Cu Interconnect Resistivity Increase



Cu Interconnect Resistivity Increase



W. Steinhogel, et al, *JAP*, 2005

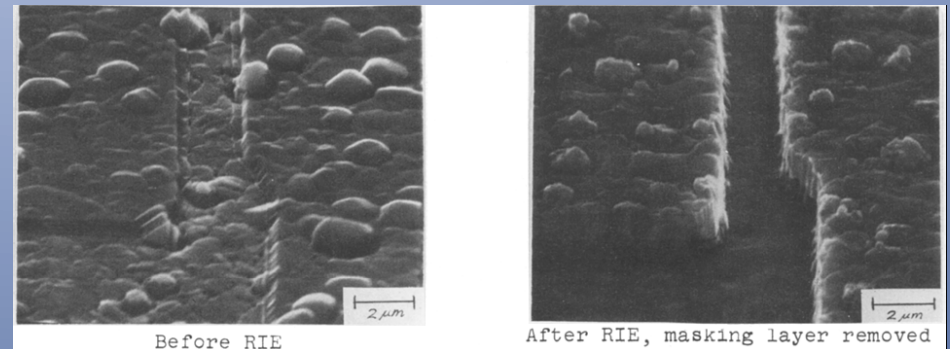
Increasing resistivity due to

- Barrier layer effect
- Scattering at surface and grain boundaries

Impacts performance and reliability of Cu interconnects.

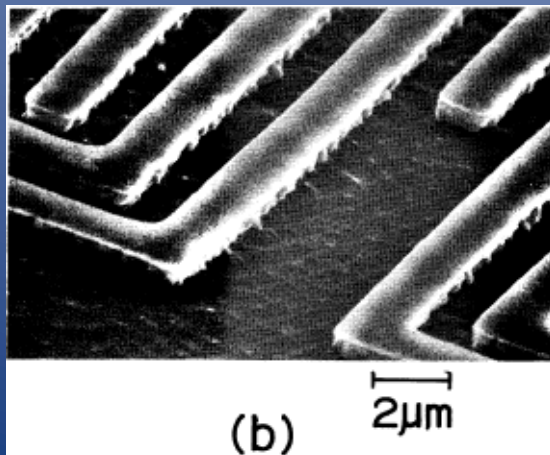
Approaches to Plasma-based Cu Etch

- RIE with CCl_4/Ar , SiCl_4/N_2 , SiCl_4/Ar , BCl_3/N_2 , BCl_3/Ar @ 250°C



CCl_4/Ar

G. C. Schwartz and P. M. Schaible, *Journal of The Electrochemical Society*, vol. 130, pp. 1777-1779, 1983.



SiCl_4/N_2

K. Ohno, M. Sato, and Y. Arita, *Japanese Journal of Applied Physics*, vol. 28, pp. L1070-L1072, 1989.

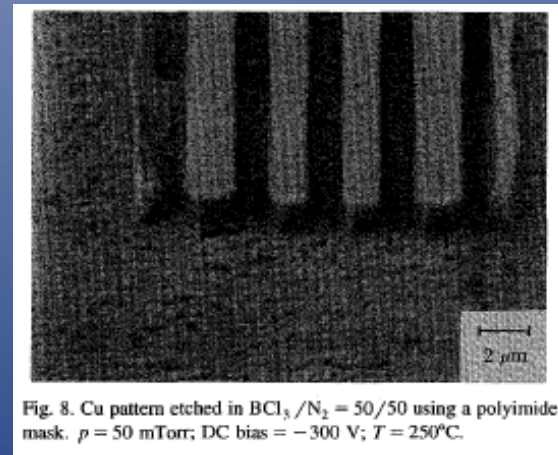


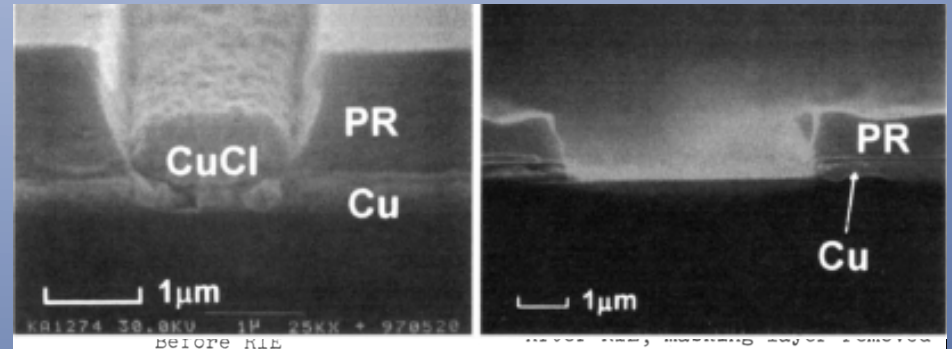
Fig. 8. Cu pattern etched in $\text{BCl}_3/\text{N}_2 = 50/50$ using a polyimide mask. $p = 50$ mTorr; DC bias = -300 V; $T = 250^\circ\text{C}$.

BCl_3/N_2

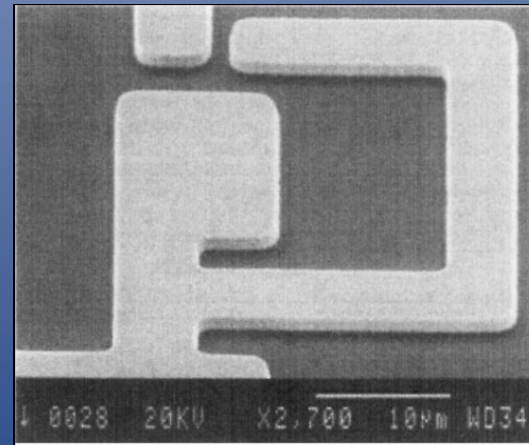
C. Steinbrüchel, *Applied Surface Science*, vol. 91, pp. 139-146, 1995.

Approaches to Plasma-based Cu Etch

- RIE with CCl_4/Ar , SiCl_4/N_2 , SiCl_4/Ar , BCl_3/N_2 , BCl_3/Ar @ 250°C
- Laser-induced & UV Photon Enhanced RIE/ICP with Cl_2 Plasma at Low Temperature



SEM photographs (a) without UV irradiation (b) with UV irradiation
C. Kang-Sik and H. Chul-Hi, *Journal of The Electrochemical Society*, vol. 145, pp. L37-L39, 1998.

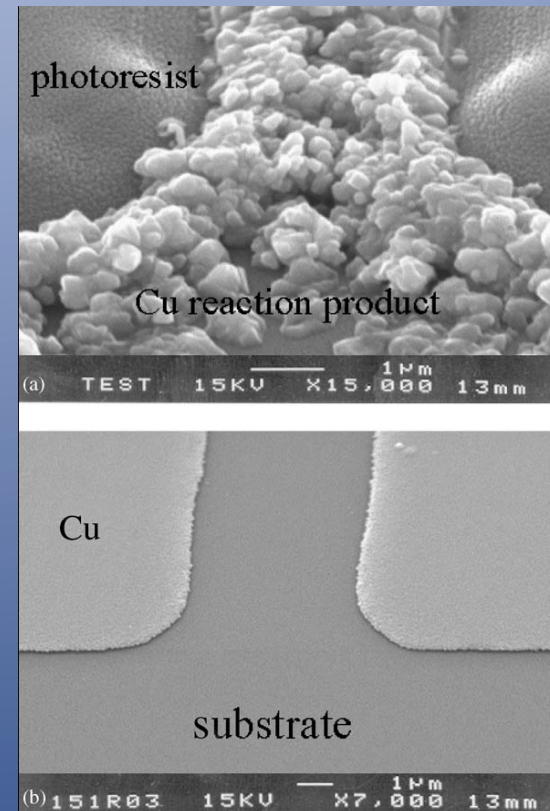


SEM micrographs of features etched into Cu layers on Si, using ICP $\text{Cl}_2:\text{Ar}$ discharges at 75°C with UV illumination.

Y. B. Hahn, S. J. Pearton, H. Cho, and K. P. Lee, *Materials Science and Engineering B*, vol. 79, pp. 20-26, 2001.

Approaches to Plasma-based Cu Etch

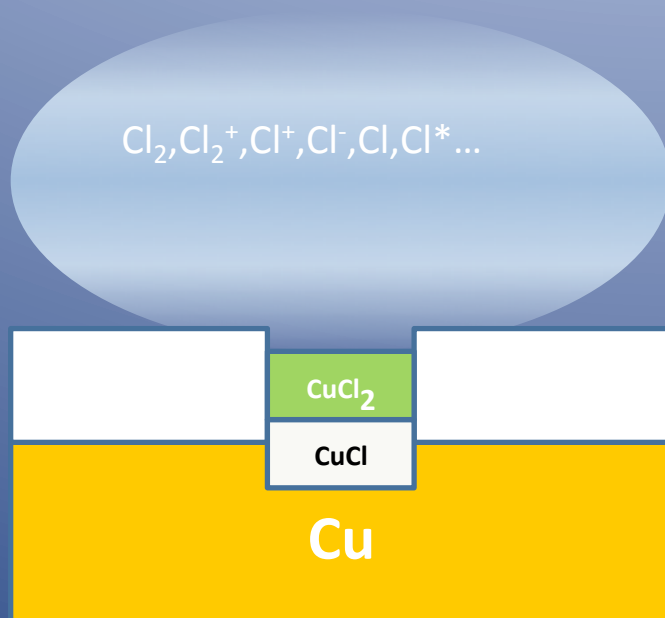
- RIE with CCl_4/Ar , SiCl_4/N_2 , SiCl_4/Ar , BCl_3/N_2 , BCl_3/Ar @ 250°C
- Laser-induced & UV Photon Enhanced RIE/ICP with Cl_2 Plasma at Low Temperature
- Low Temperature vacuum/liquid process sequence: Plasma of HCl , Cl_2 or HBr followed by immersion in a dilute HCl solution



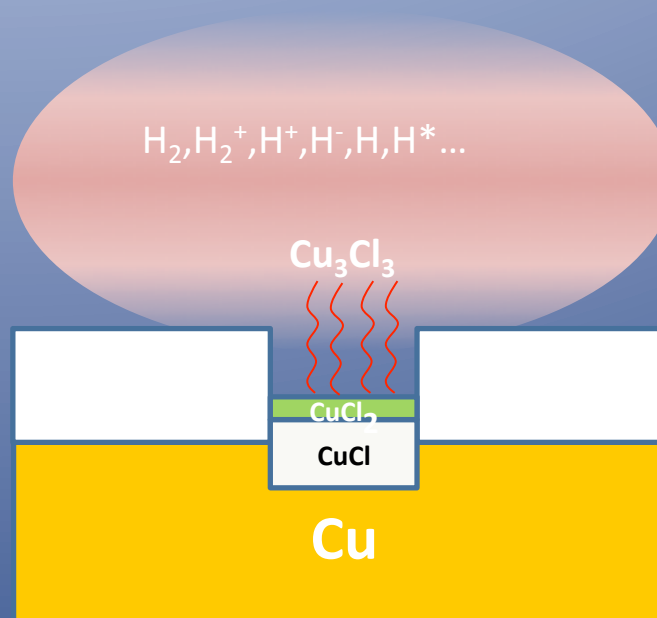
Photoresist patterned Cu layer after Cl_2 plasma, exposure and (b) after removal of CuCl_x and photoresist

Thermodynamic Justification of Two-step plasma etch of Cu

Chlorine Plasma



Hydrogen Plasma



- If H atoms are present in the Cu-Cl system:

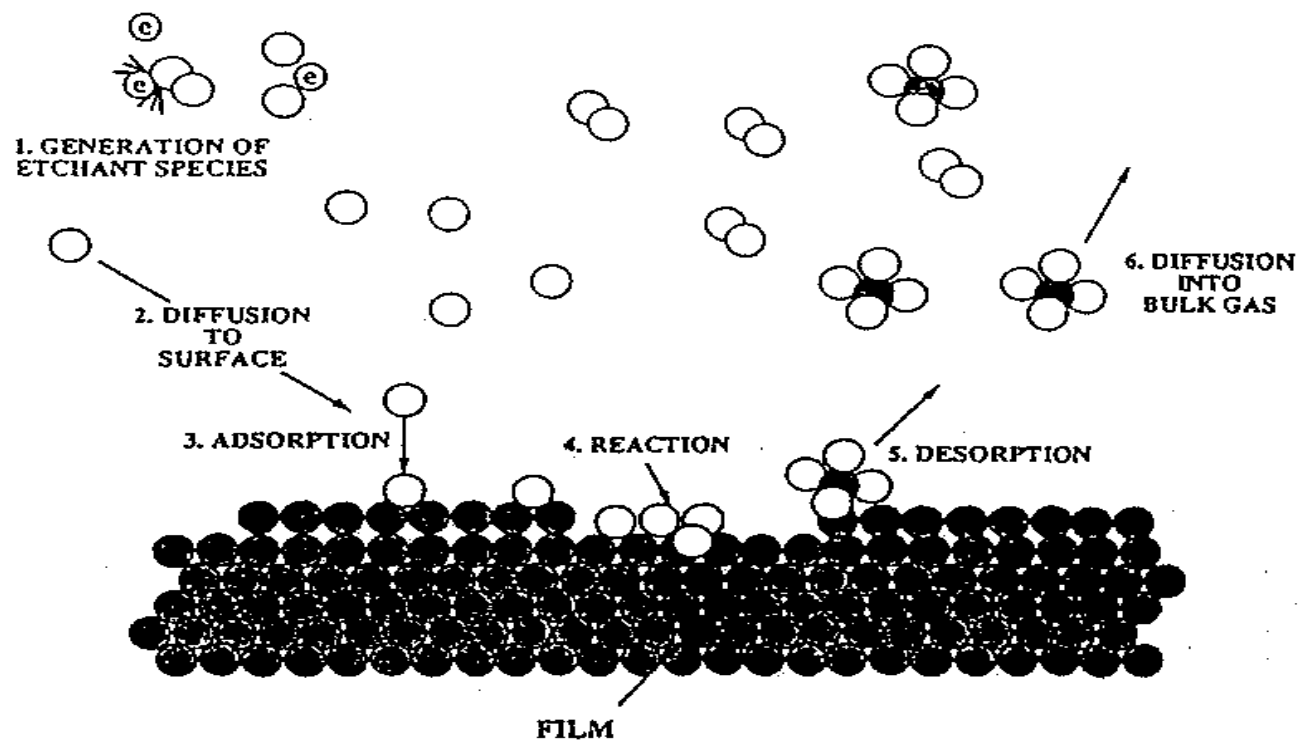
$$3 \text{CuCl}_2 (\text{c}) + 3 \text{H} (\text{g}) = \text{Cu}_3\text{Cl}_3 (\text{g}) + 3 \text{HCl} (\text{g})$$
- Cu_3Cl_3 partial pressure \uparrow as the temperature \downarrow

Elementary process at the surfaces immersed in low pressure plasma

- **Ion-Surface Interactions:**
 - Neutralization and secondary electron emission
 - Sputtering
 - Ion Induced Chemical Reactions
- **Electron-Surface Interactions**
 - Secondary Electron Emission
 - Electron Induced Chemical Reactions
- **Radical or Atom Surface Interactions**
 - Surface Etching
 - Film Deposition

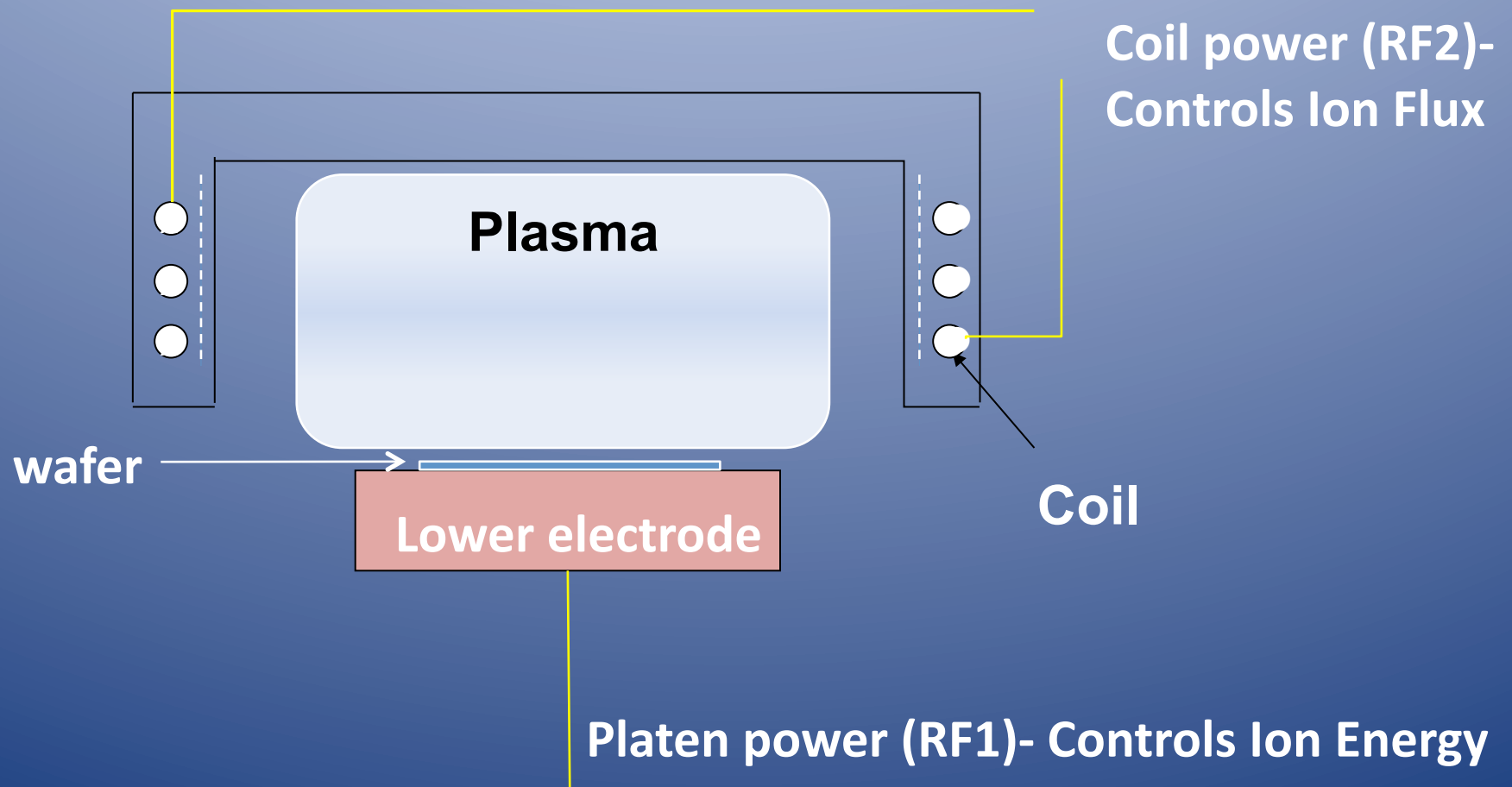
ETCHING PARAMETERS

Ideally, plasma or glow discharge etching can be broken down into six steps; if any of these steps does not occur, etching terminates.



from Mucha, Hess and Aydil, p. 386

Inductively Coupled Plasma Reactor



Two-step plasma etch of Cu

Etch stack:

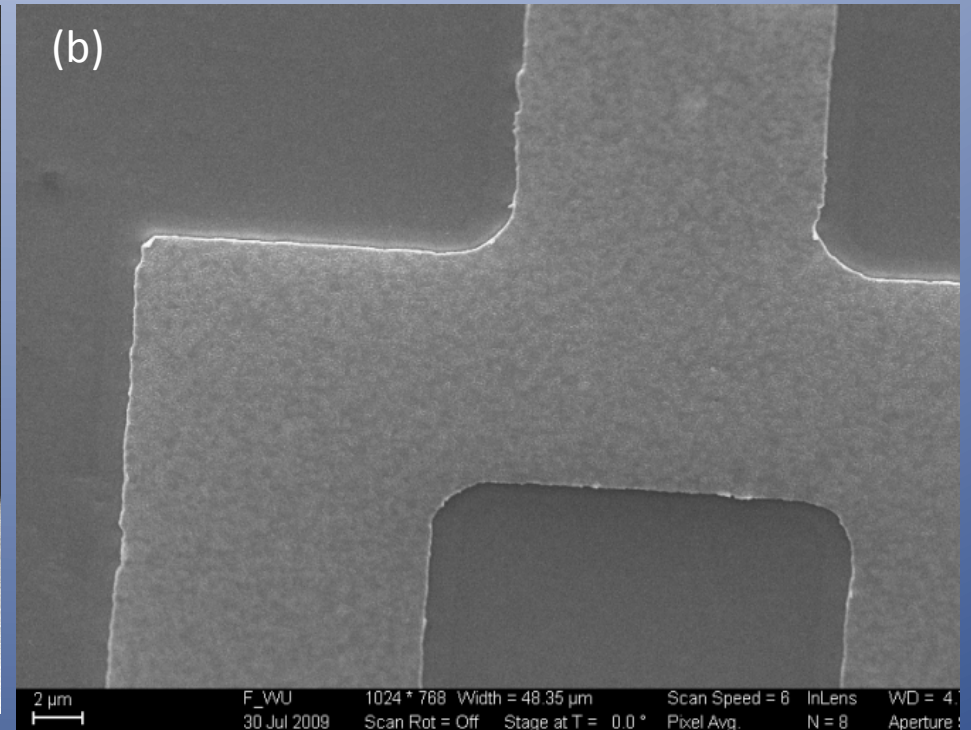
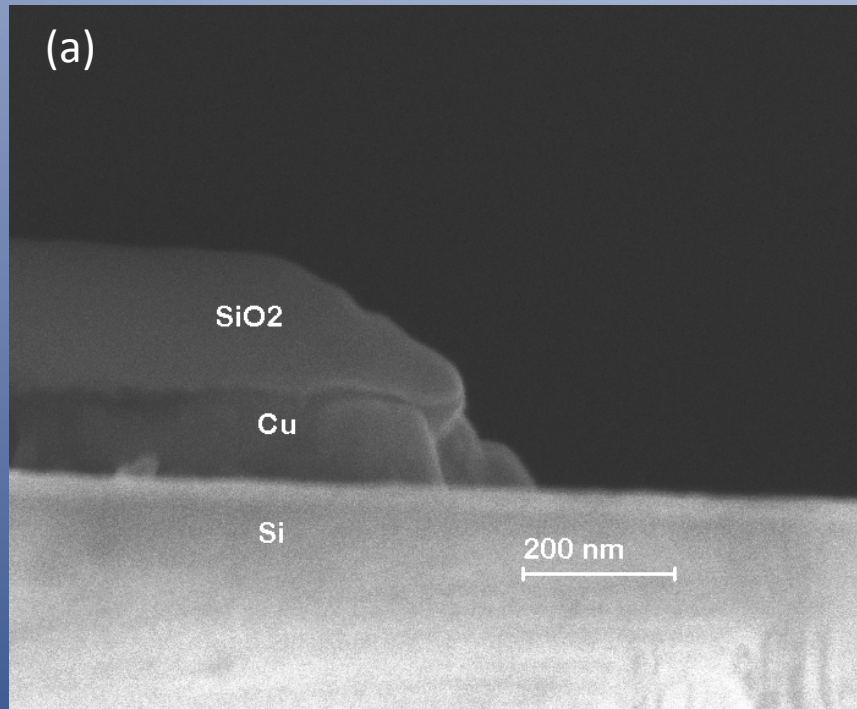
n type Si wafer

8-9 nm Ti adhesion layer

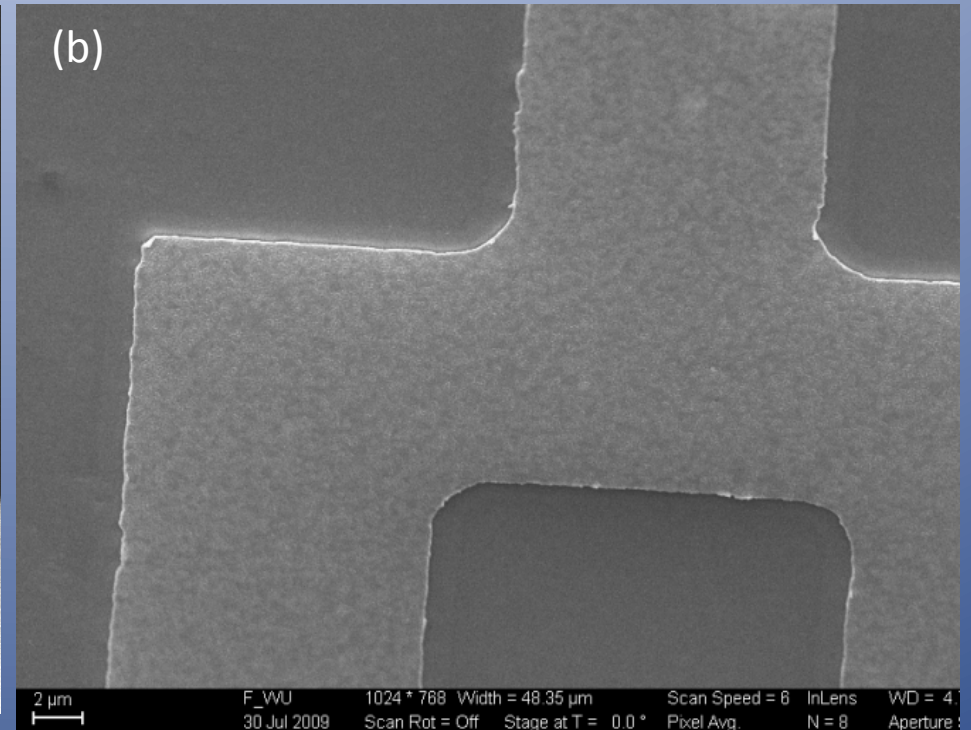
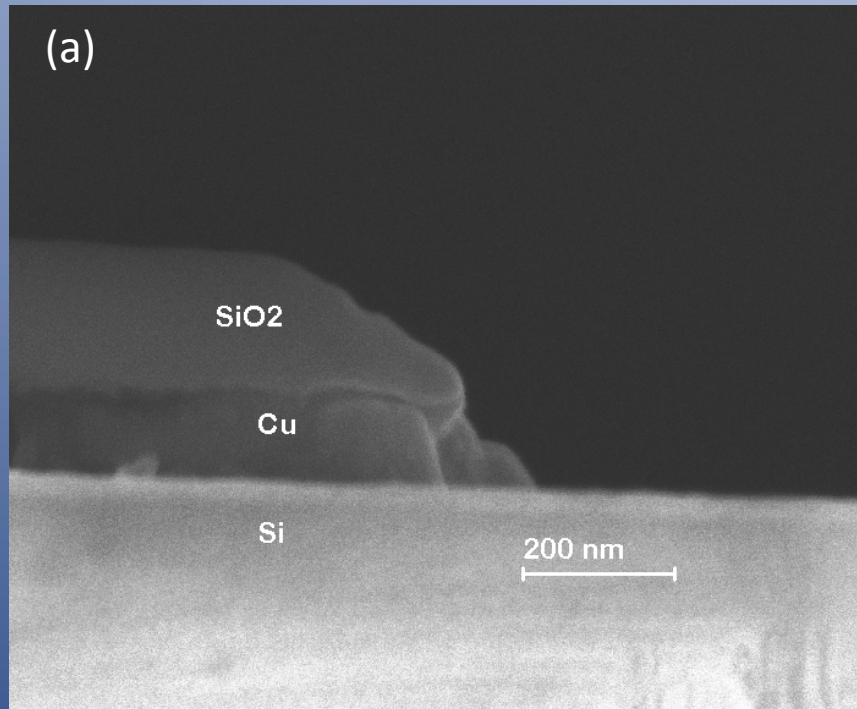
100 nm Cu layer

150 nm SiO₂ hard mask

Two-step plasma etch of Cu

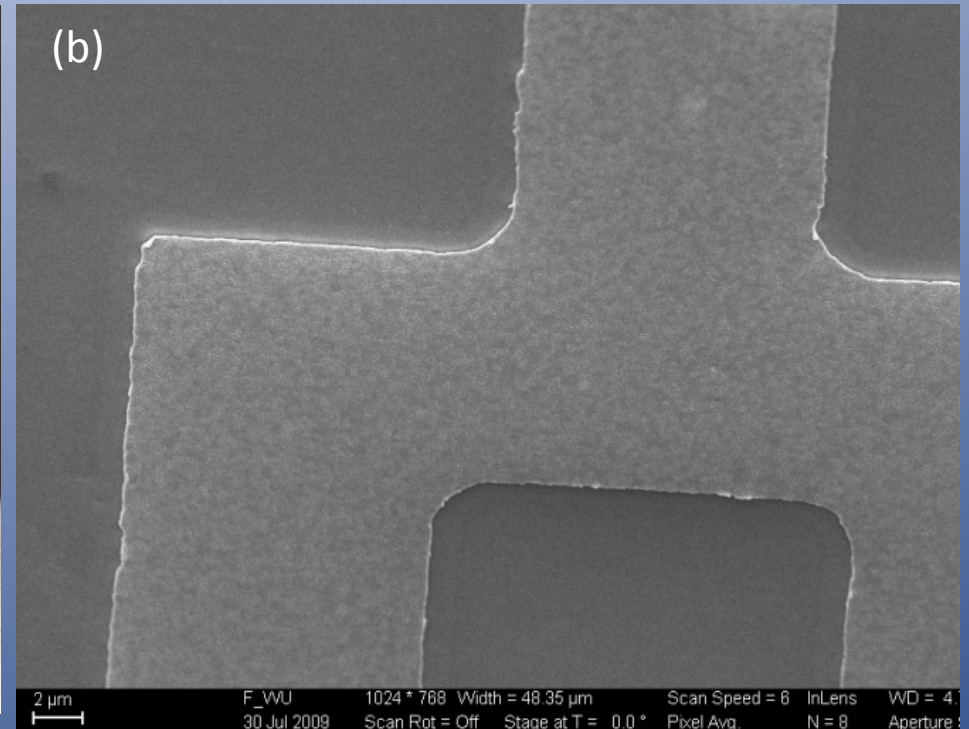
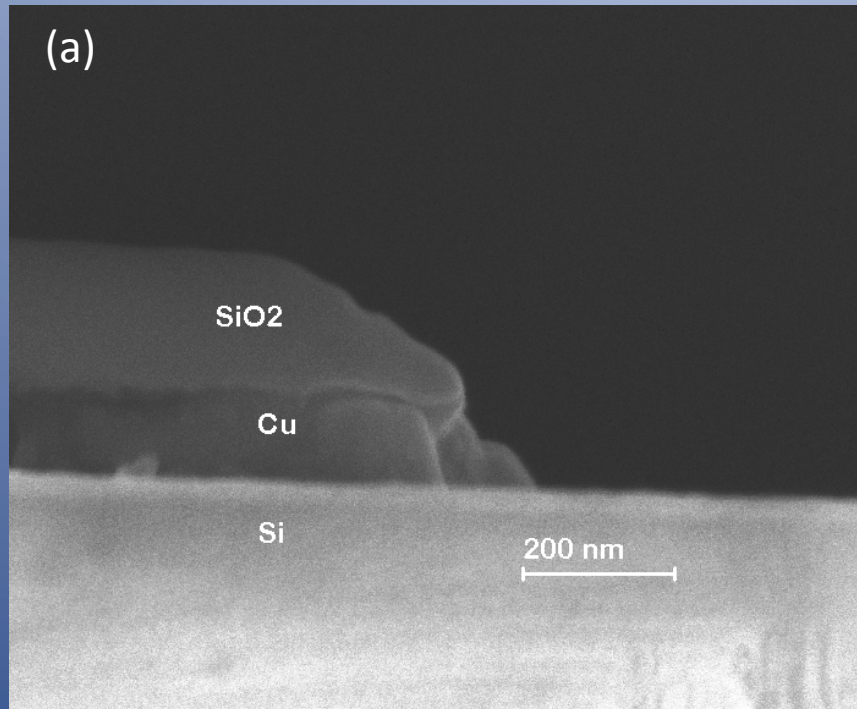


Two-step plasma etch of Cu



- Hydrogen plasma is the limiting step

Two-step plasma etch of Cu



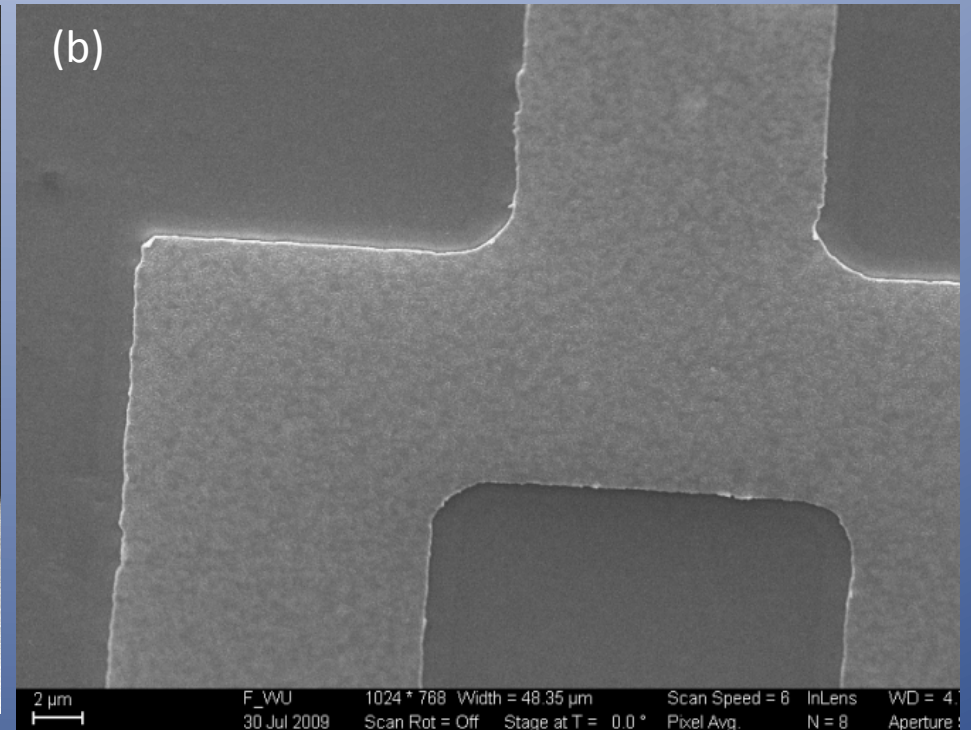
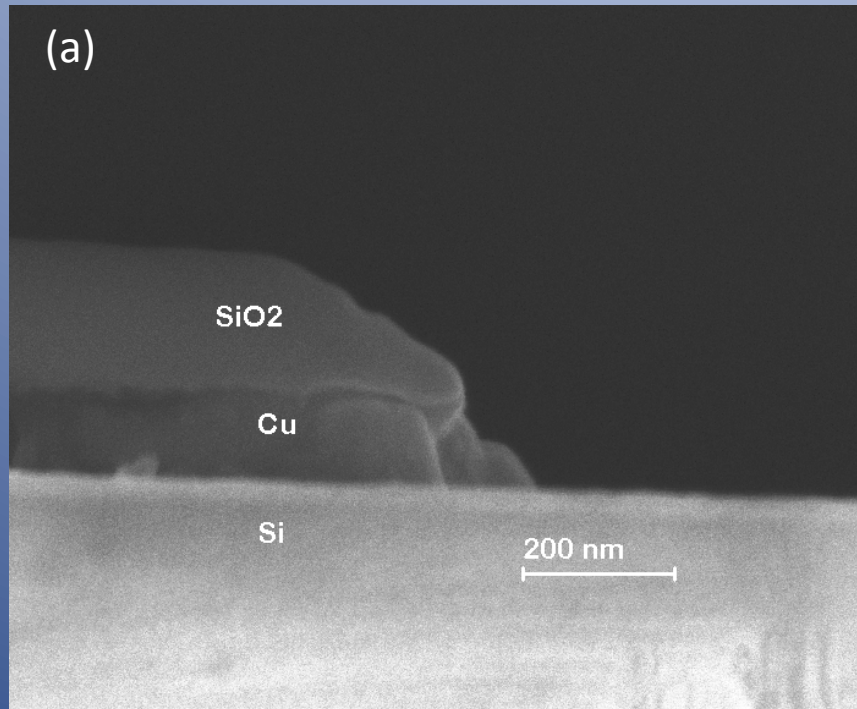
Etch Conditions:

Plasma Therm ICP reactor: 30 sec Cl₂ plasma + 2 min H₂ plasma, **10 ° C**

(a)12 cycles ; (b)6 cycles: Ar addition to the H₂ plasma

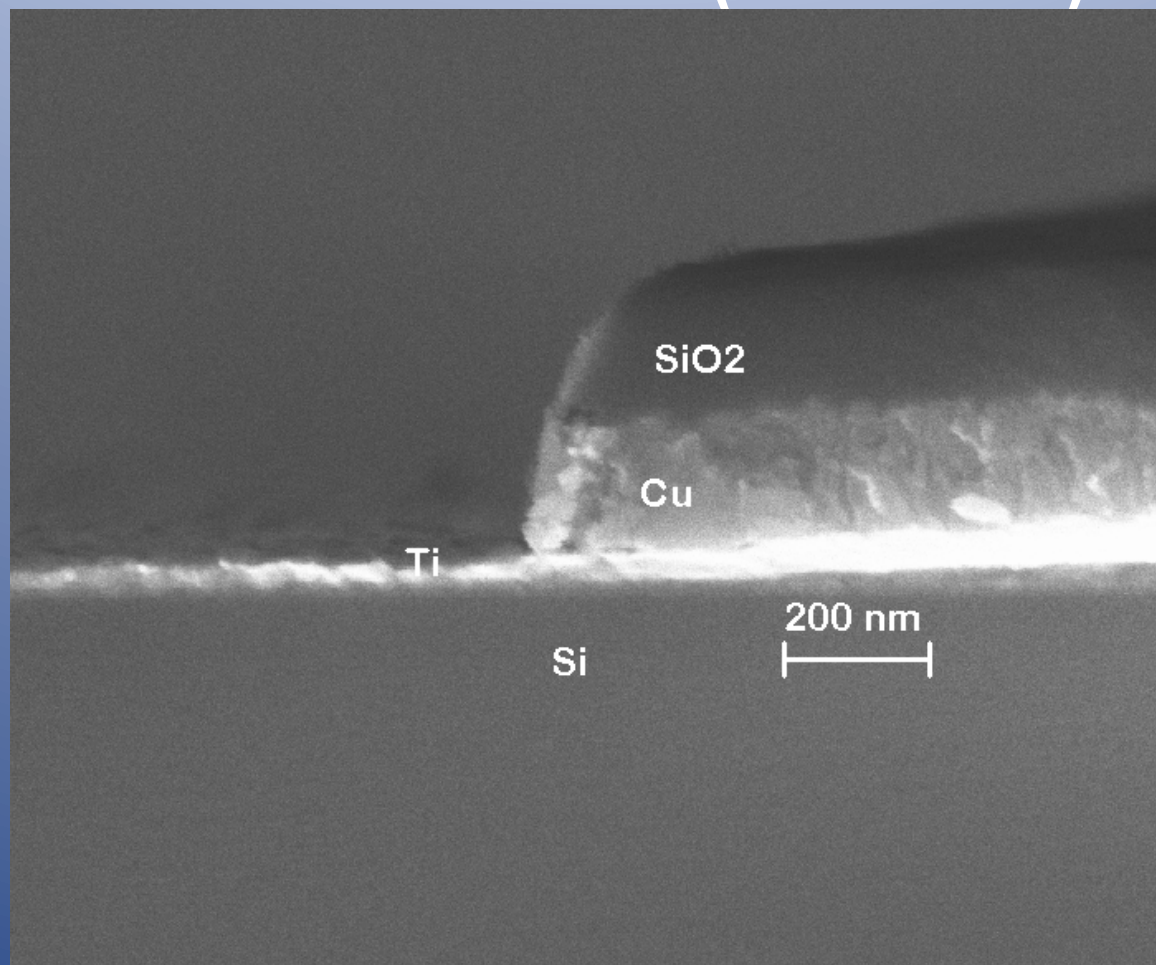
F. Wu, G. Levitin, and D. W. Hess, *Journal of The Electrochemical Society*, vol. 157, pp. H474- 42 H478, 2010.

Two-step plasma etch of Cu



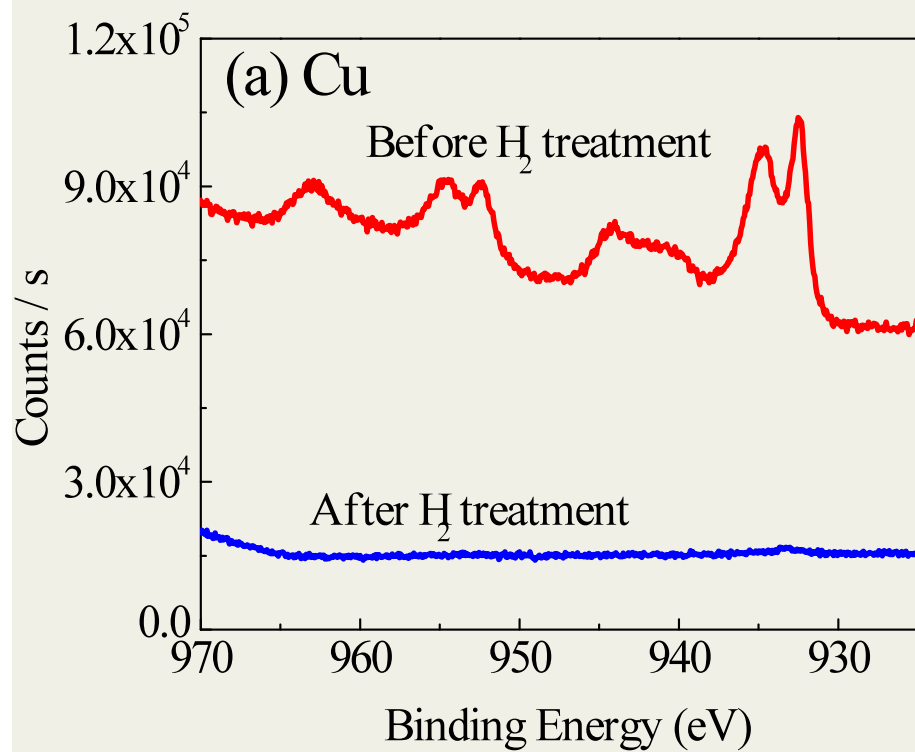
- Hydrogen plasma is the limiting step

H₂ plasma etch of Cu (100 nm)

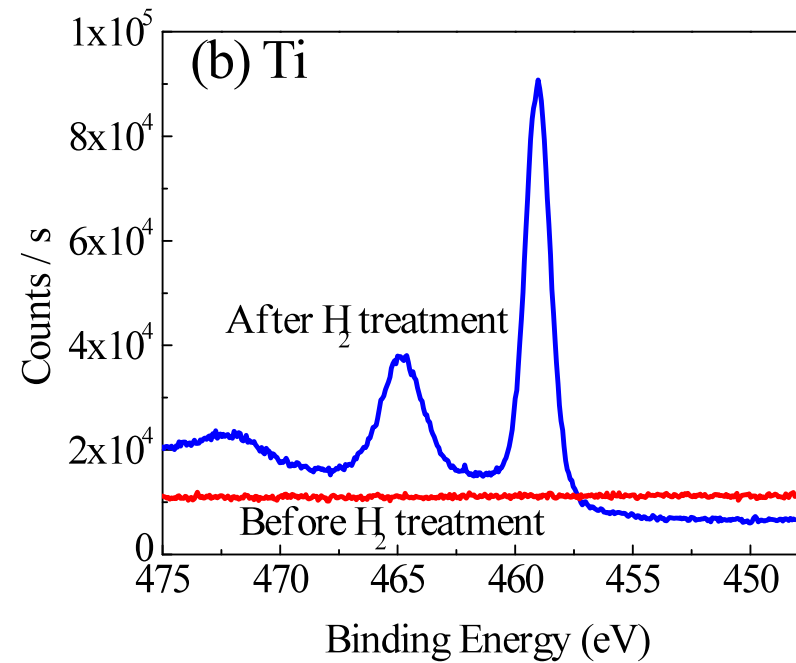
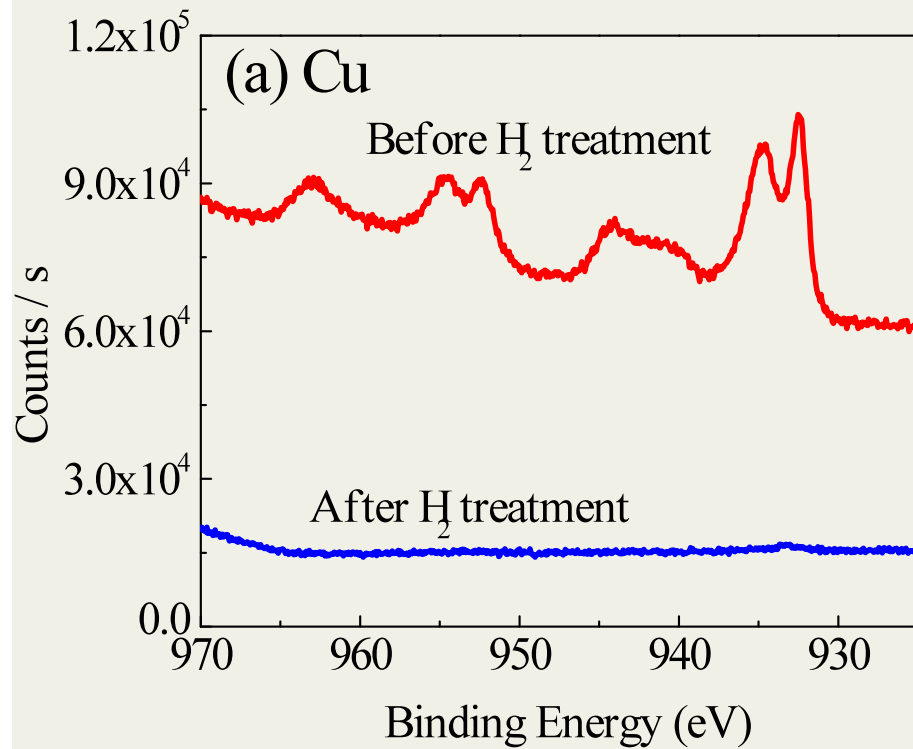


- Etch rate: 13 nm/ min
- Plasma Therm ICP reactor, 10 °C, 20 mtorr, 50 sccm H₂, RF1/RF2=100W/500W

XPS analysis

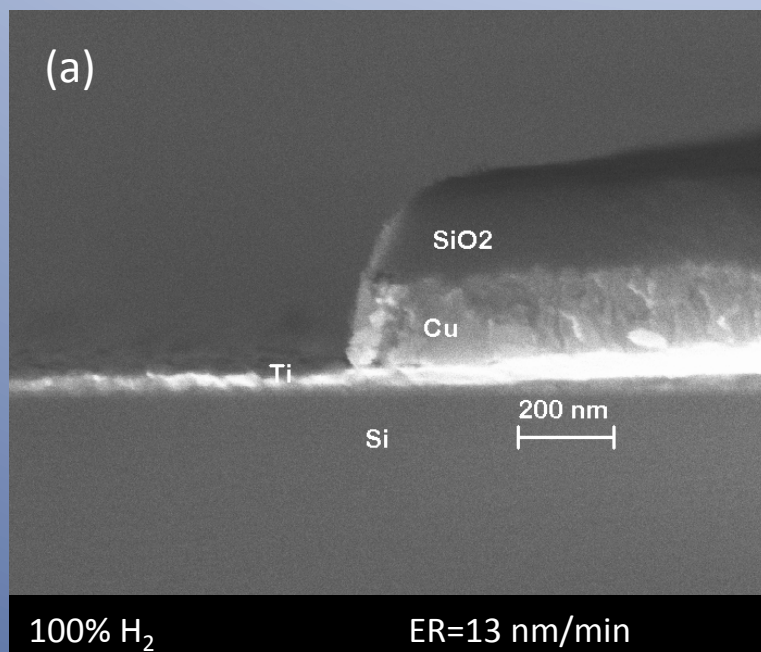


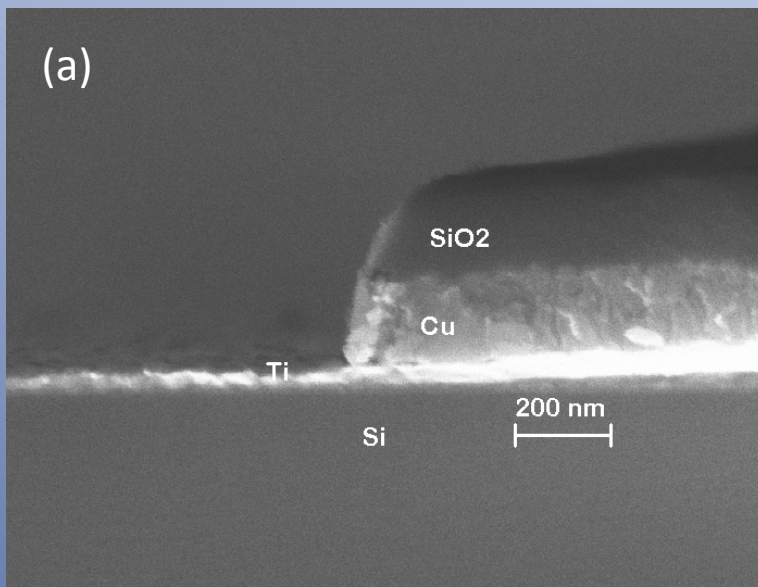
XPS analysis



Mechanistic studies

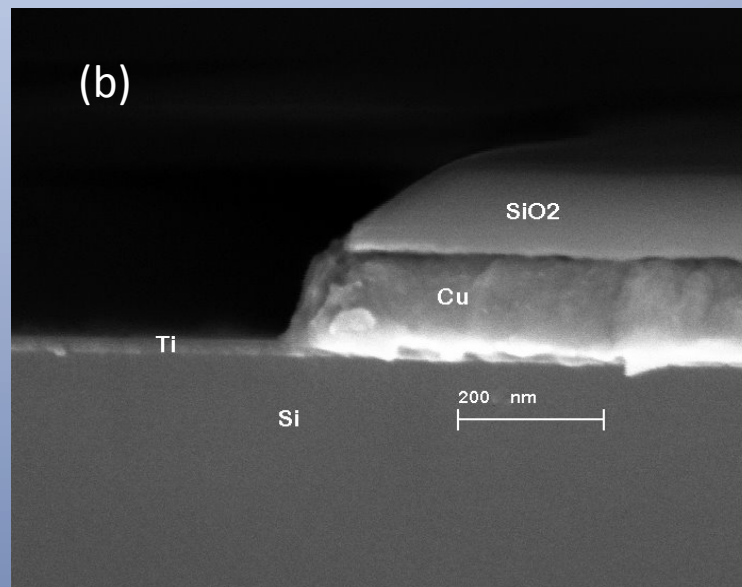
- Chemical etch vs Sputtering





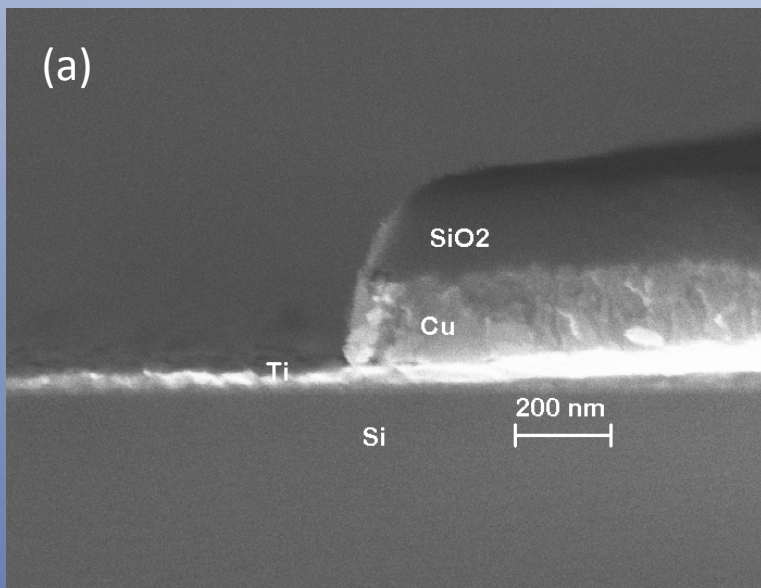
100% H₂

ER=13 nm/min



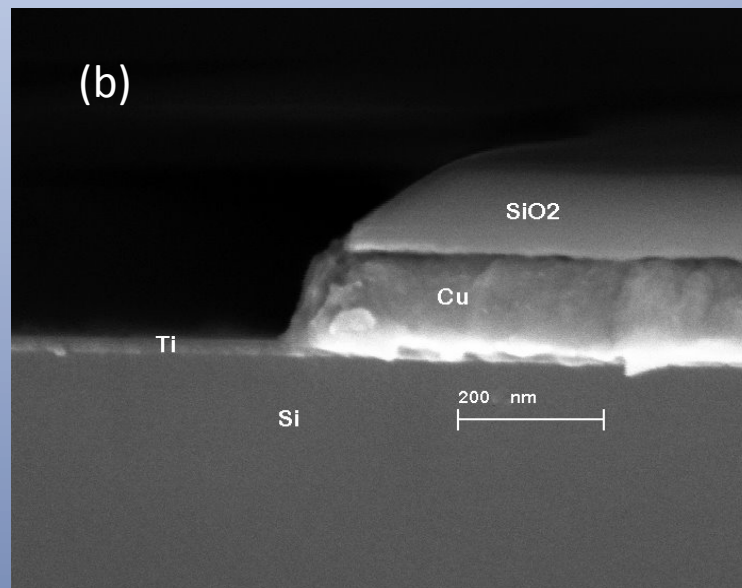
H₂ : Ar = 1 : 1

ER=16 nm/min



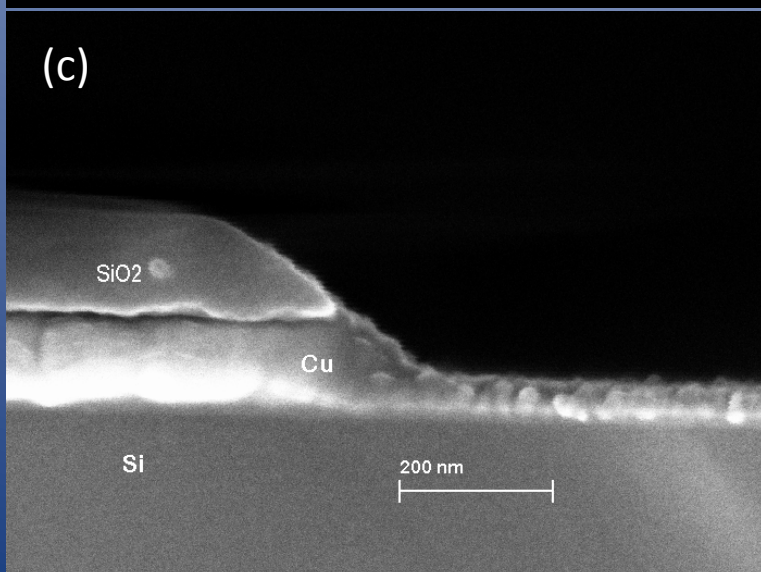
100% H₂

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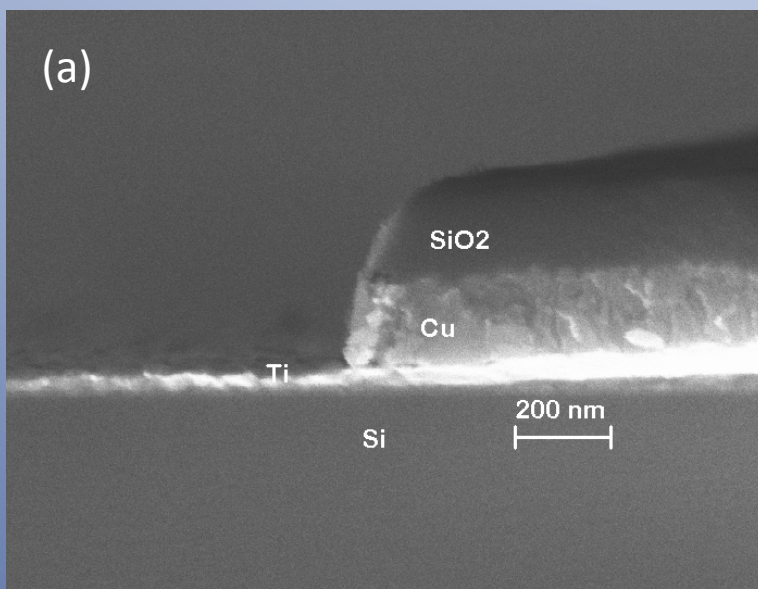
H₂ : Ar = 1 : 1

ER=16 nm/min



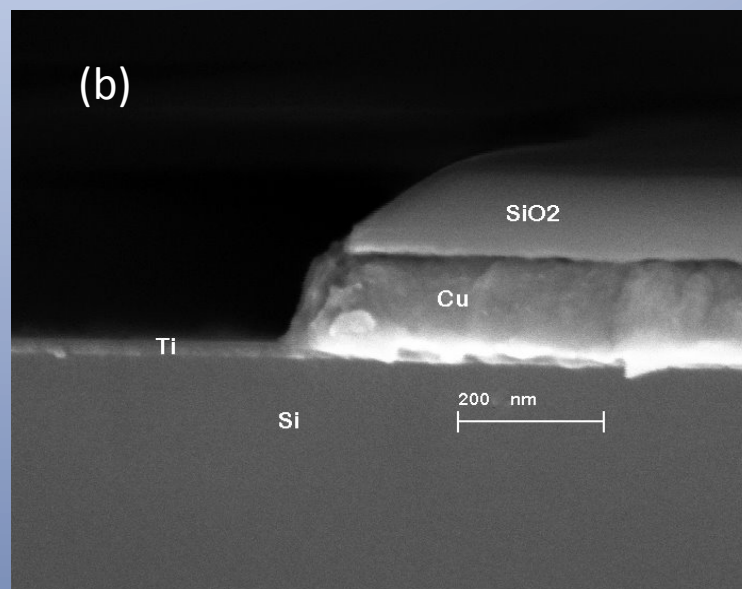
H₂ : Ar = 1 : 4

ER=10 nm/min



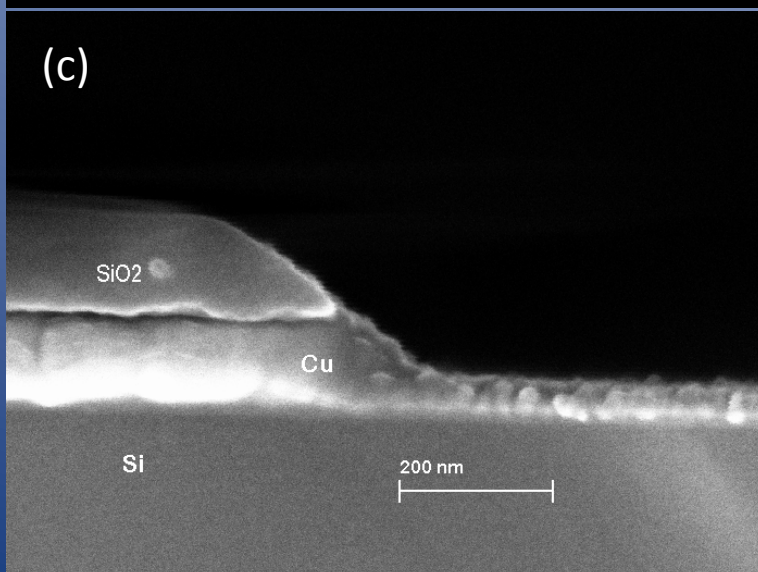
100% H₂

ER=13 nm/min



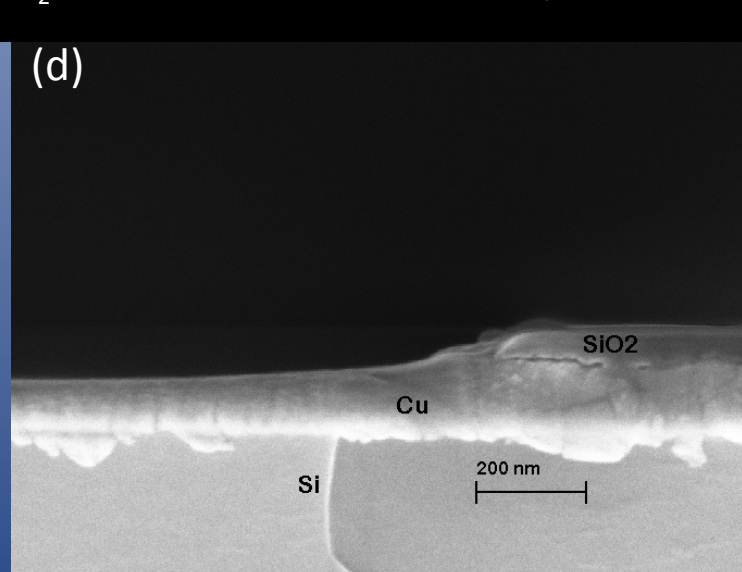
H₂ : Ar = 1 : 1

ER=16 nm/min



H₂ : Ar = 1 : 4

ER=10 nm/min



100% Ar

ER=4 nm/min

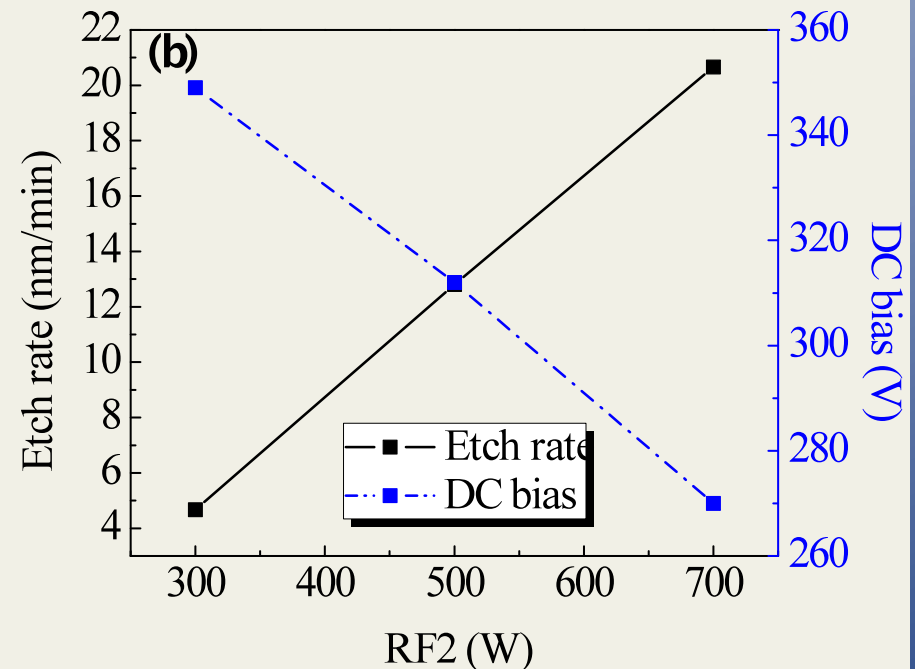
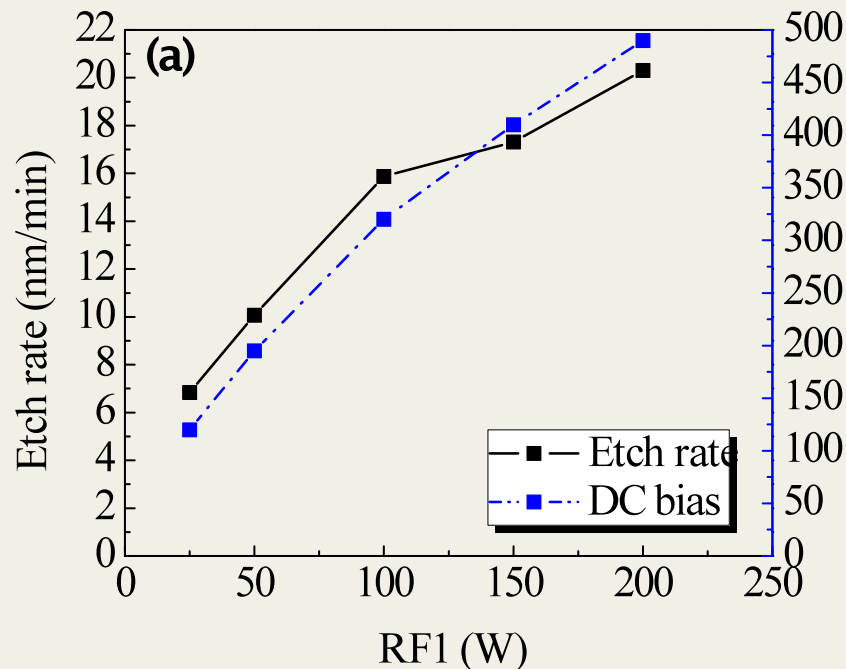
Chemical Component: Etch Products

Possible etch products:

Copper Compounds

CuH	Thermally unstable (decomposes $<100\text{ }^{\circ}\text{C}$)
CuH ₂	Unstable
CuH ₂ ⁻	Possibly stable at some conditions
Cu ₂ O	Melting point = $1235\text{ }^{\circ}\text{C}$
CuO	Melting point = $1201\text{ }^{\circ}\text{C}$

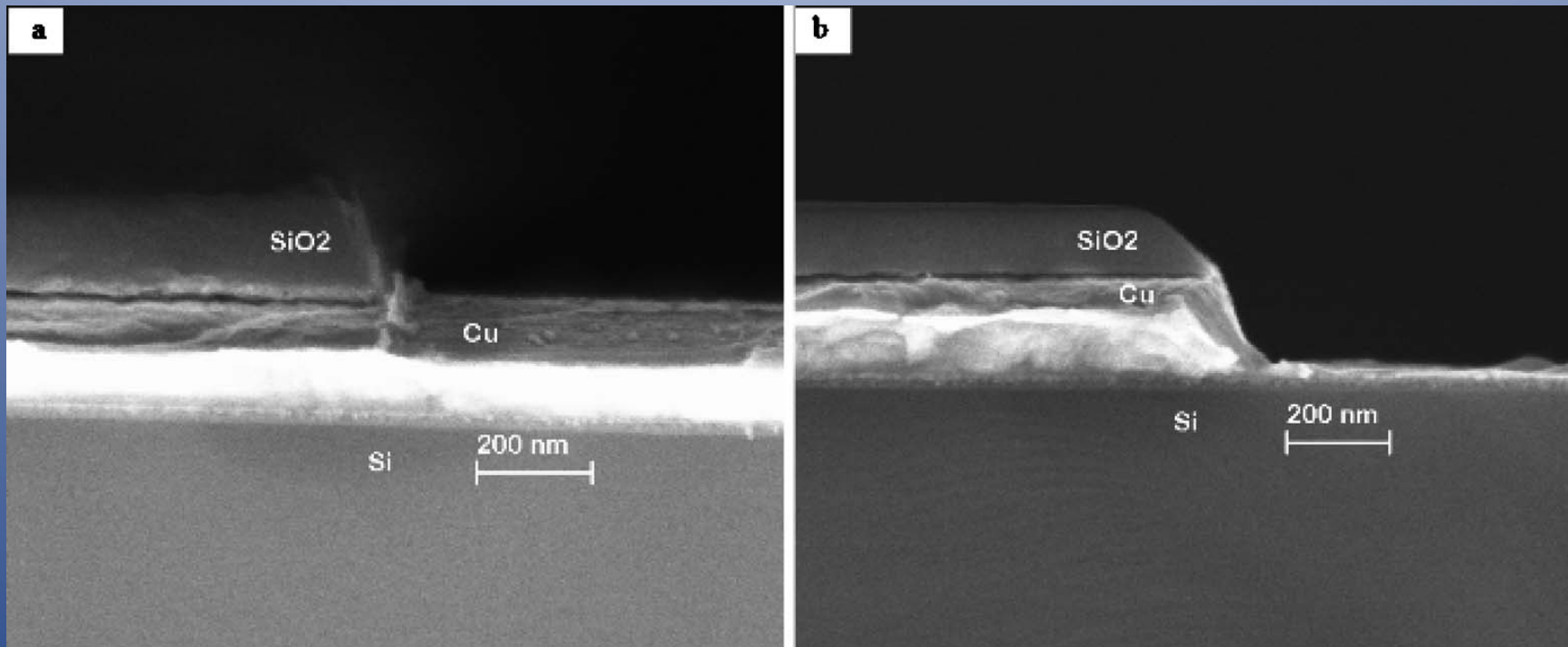
Physical component: Ion Bombardment



- Cu etch rate vs.
 - (a) platen power (RF1) when RF2 = 500W controls ion energy
 - (b) coil power (RF2) when RF1 = 100W controls ions flux
- DC bias directly proportional to ion energy

F. Wu, G. Levitin, and D. W. Hess, *The Journal of Vacuum Science and Technology B*, vol. 29, pp. 011013-1-7, 2010.

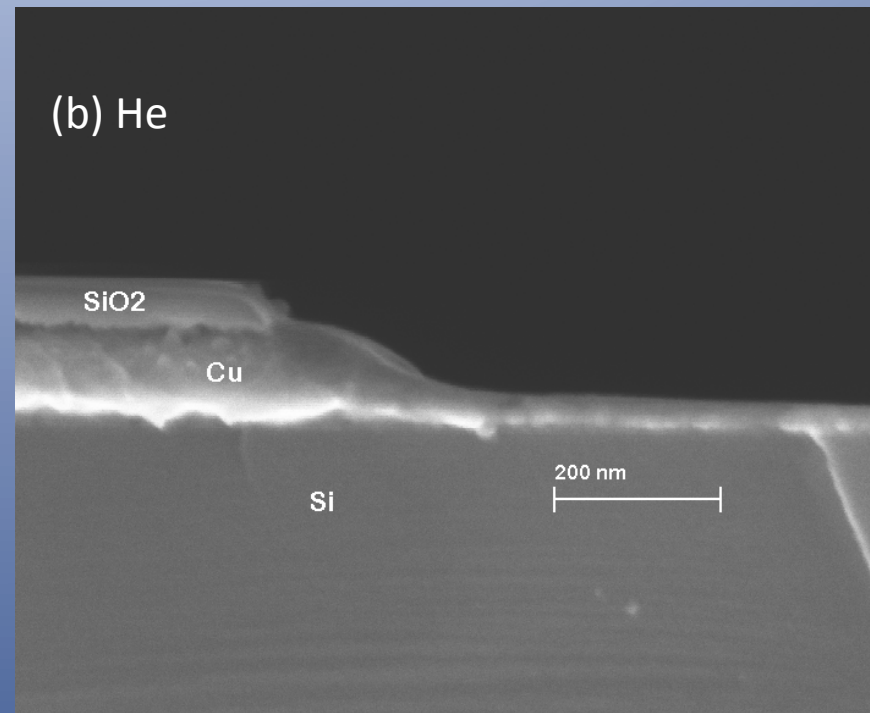
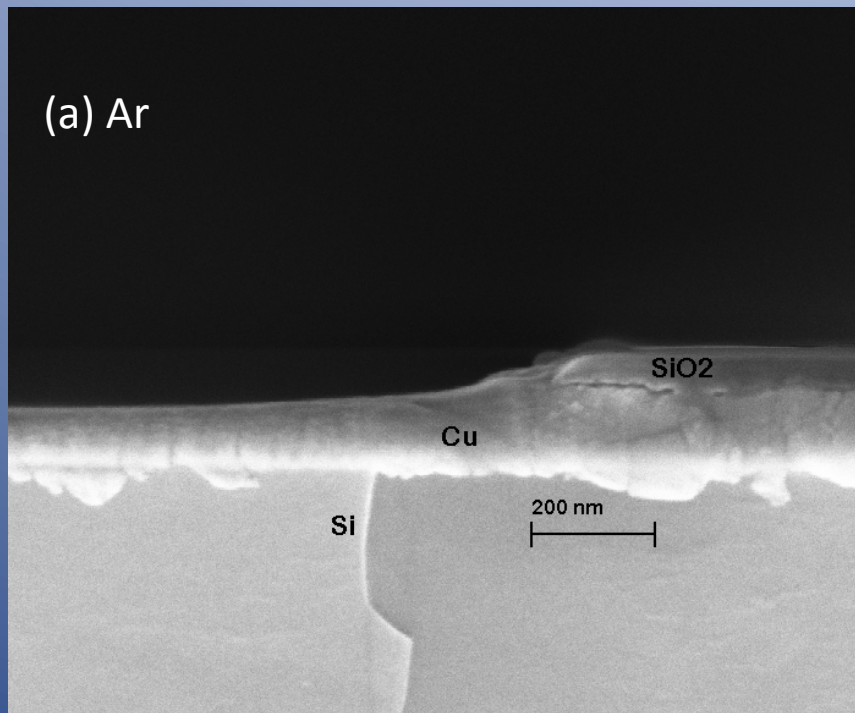
Physical component: Ion Bombardment



Cross sectional SEMs of SiO₂ masked, 180 nm Cu films a before and b after 8 min of H₂ plasma under the conditions rf1=100 W, rf2=700 W, etch rate 20 nm/min

F. Wu, G. Levitin, and D. W. Hess, *The Journal of Vacuum Science and Technology B*, vol. 29, pp. 011013-1-7, 2010.

Comparison of Ar and He as Cu Etchants



- (a) Ar ($\sim 4\text{nm/min}$); (b) He ($\sim 10\text{ nm/min}$)
- Etch rate: $\text{H}_2 > \text{He} > \text{Ar}$
- SiO₂ ablation; Anisotropy degradation.

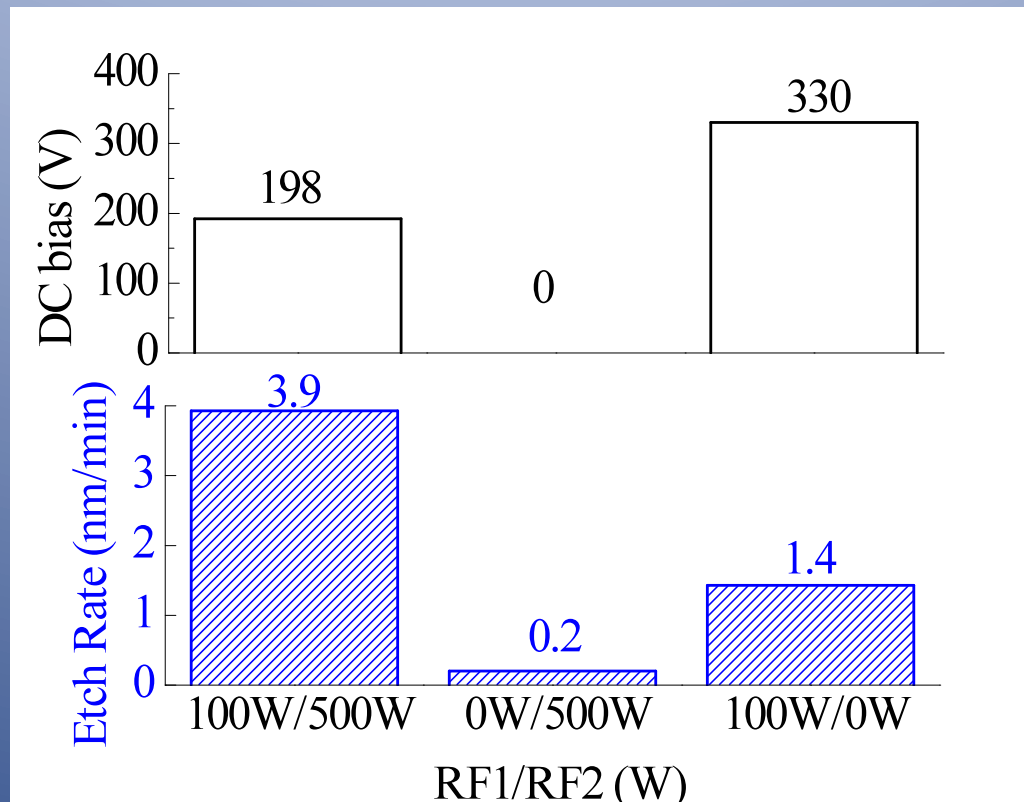
Physical Component: UV Photons

Atomic emission lines (in angstroms) of H₂, Ar, He and Cl in the high energy regime (from Grotrian Diagrams). Asterisk indicates the highest intensity in each column.

H	Ar	He	Cl
972.54	876.06	537.024	1201.4
1025.83*	894.30	584.331*	1347.3/1351.7/1363.5
1215.68	1048.22*	591.420	1379.6/1389.9/1396.5*
	1066.66		

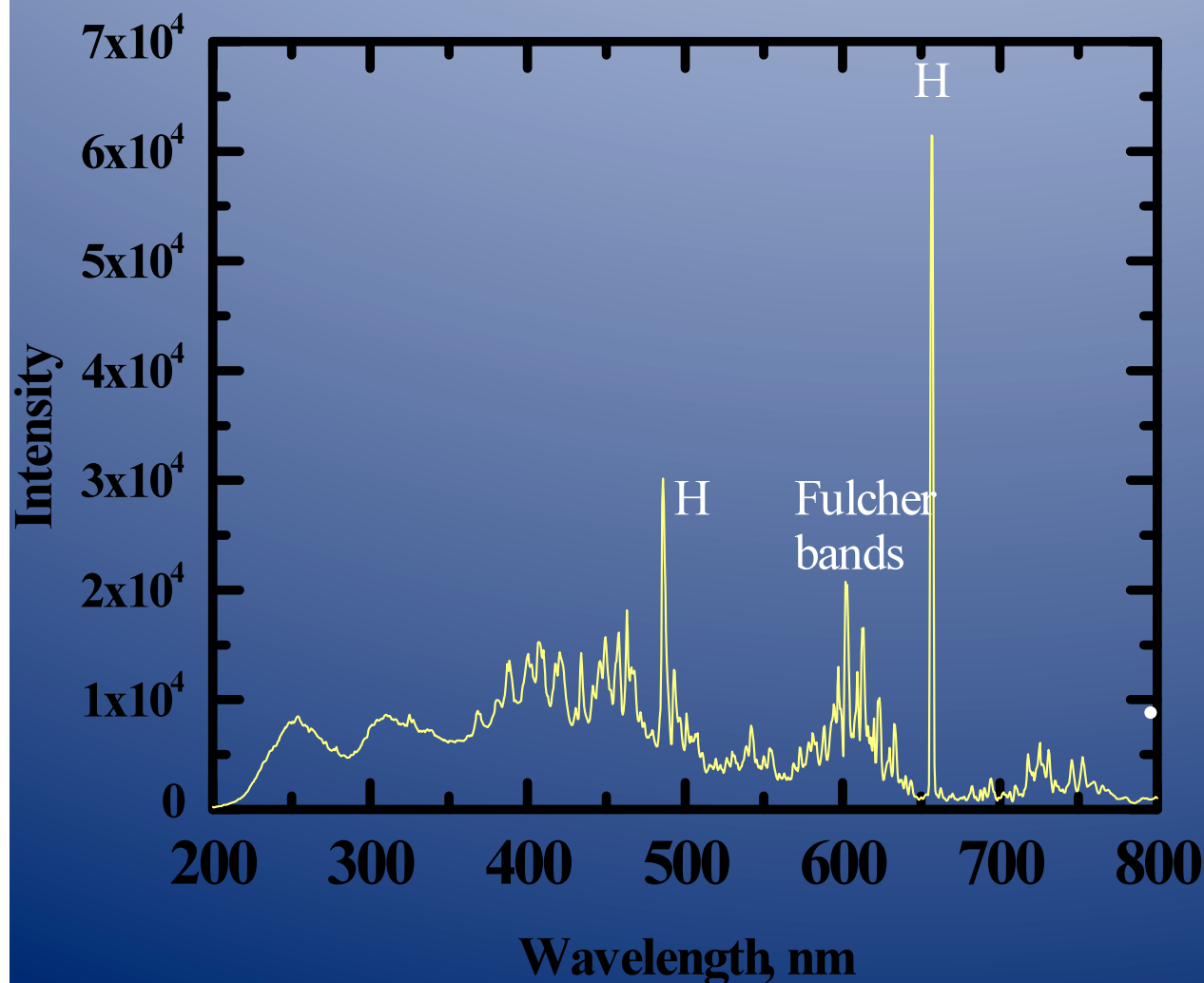
- UV wavelength range;
- He plasma: source of VUV photons

Ion bombardment vs. Chemical Reaction



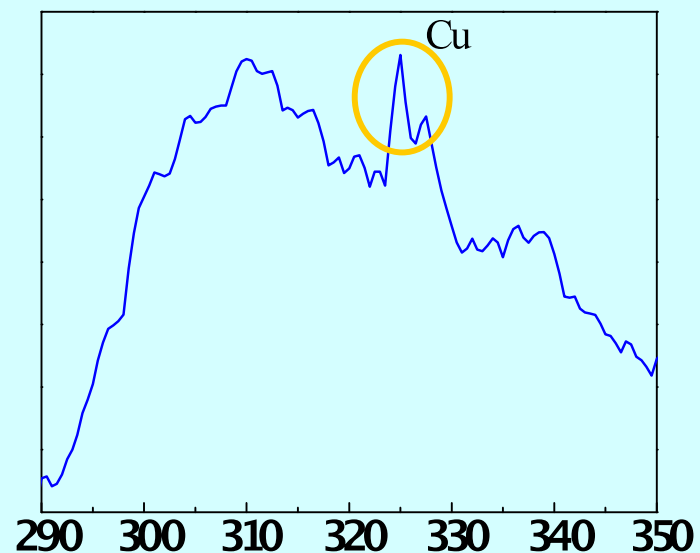
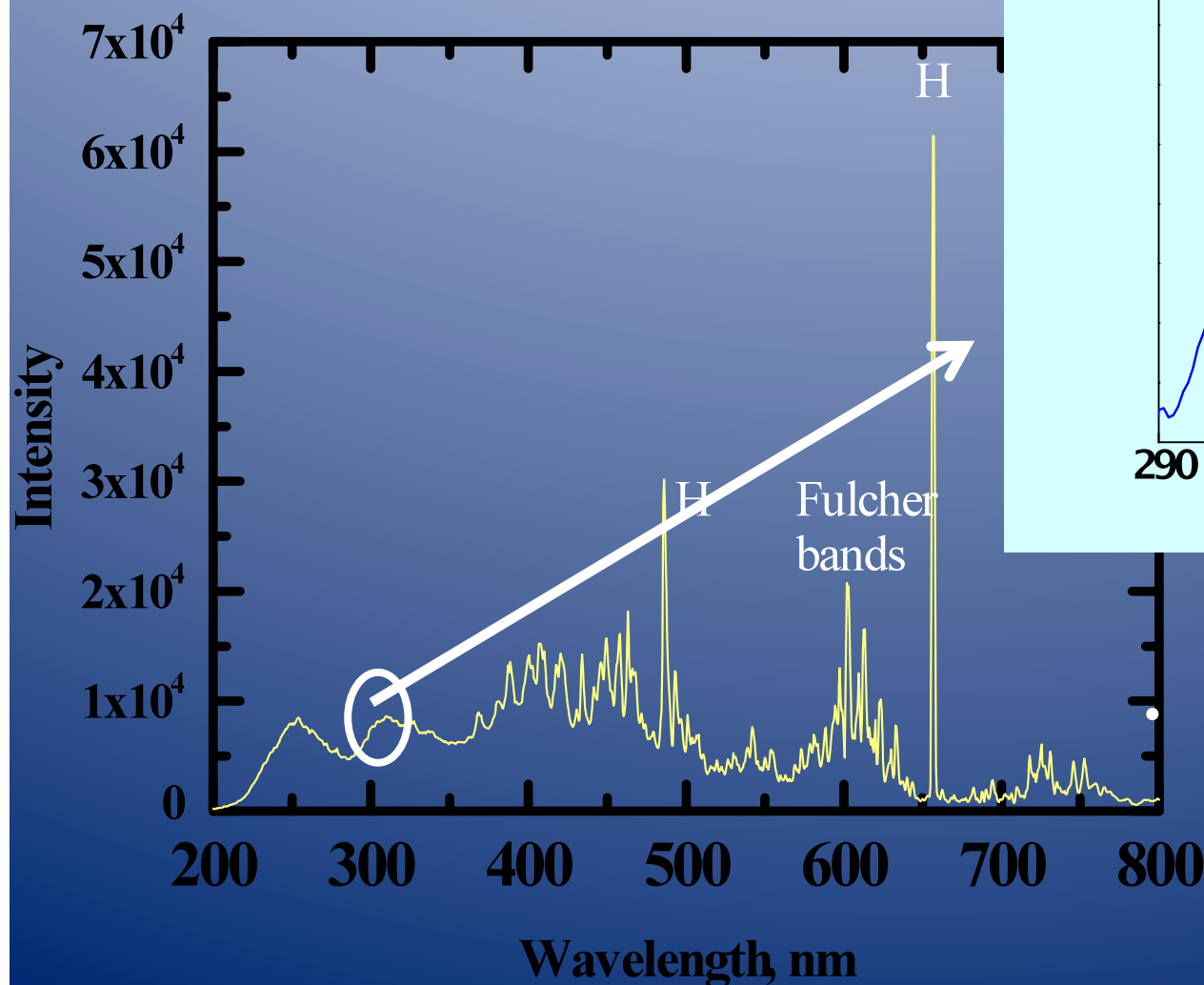
- STS AOE reactor : 20 mtorr, 50 sccm H₂, **20 °C**
- RF1: platen power ; RF2: coil power
- Both ion bombardment and chemical reaction contribute

Optical Emission Spectra (OES) of H₂ Plasma



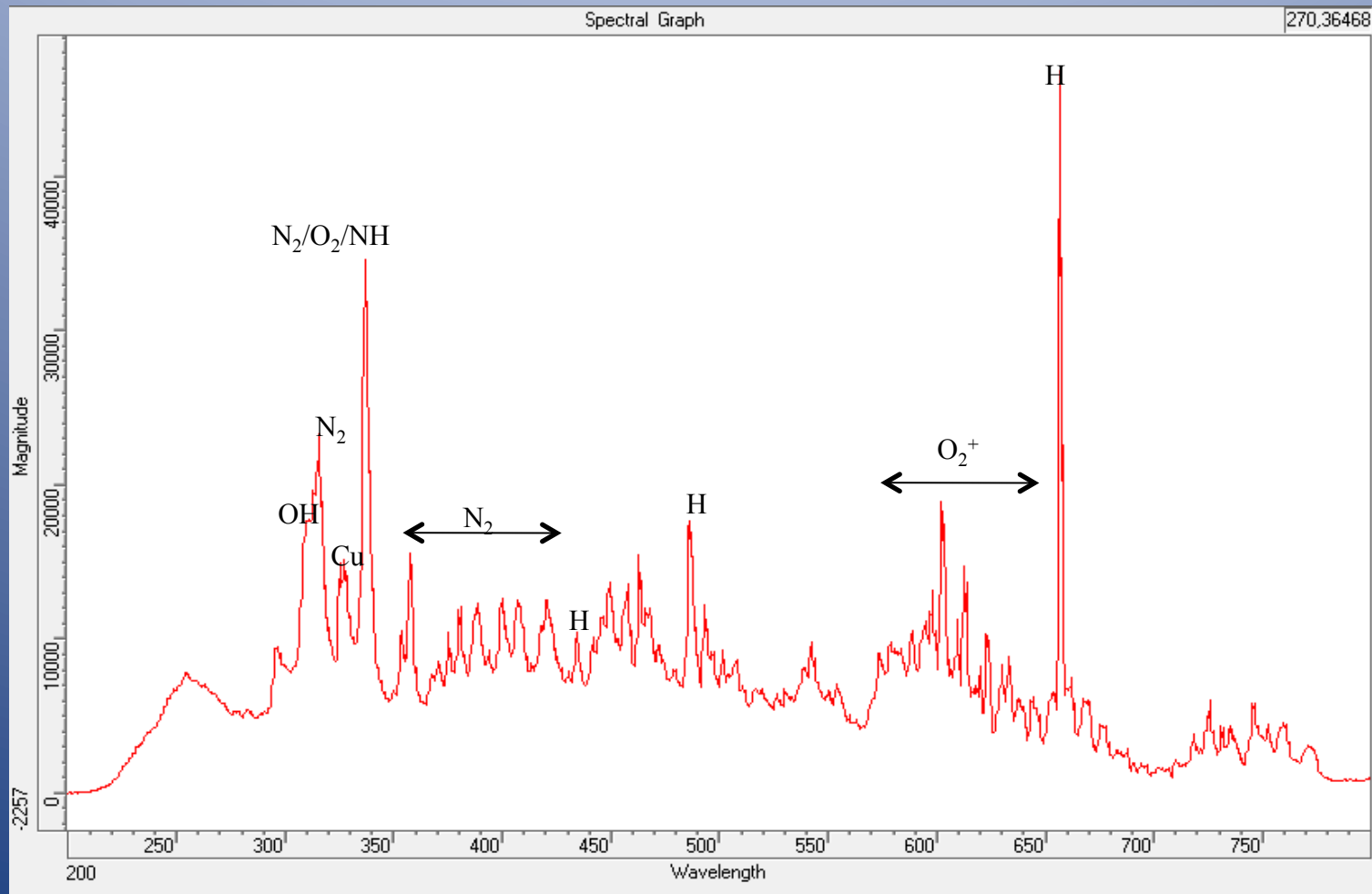
Oxford PlasmaLab ICP
reactor :
20 mtorr, 60 sccm H₂, 10 °C

Optical Emission Spectra (OES) of H₂ Plasma



Oxford PlasmaLab ICP
reactor :
20 mtorr, 60 sccm H₂, 10 °C

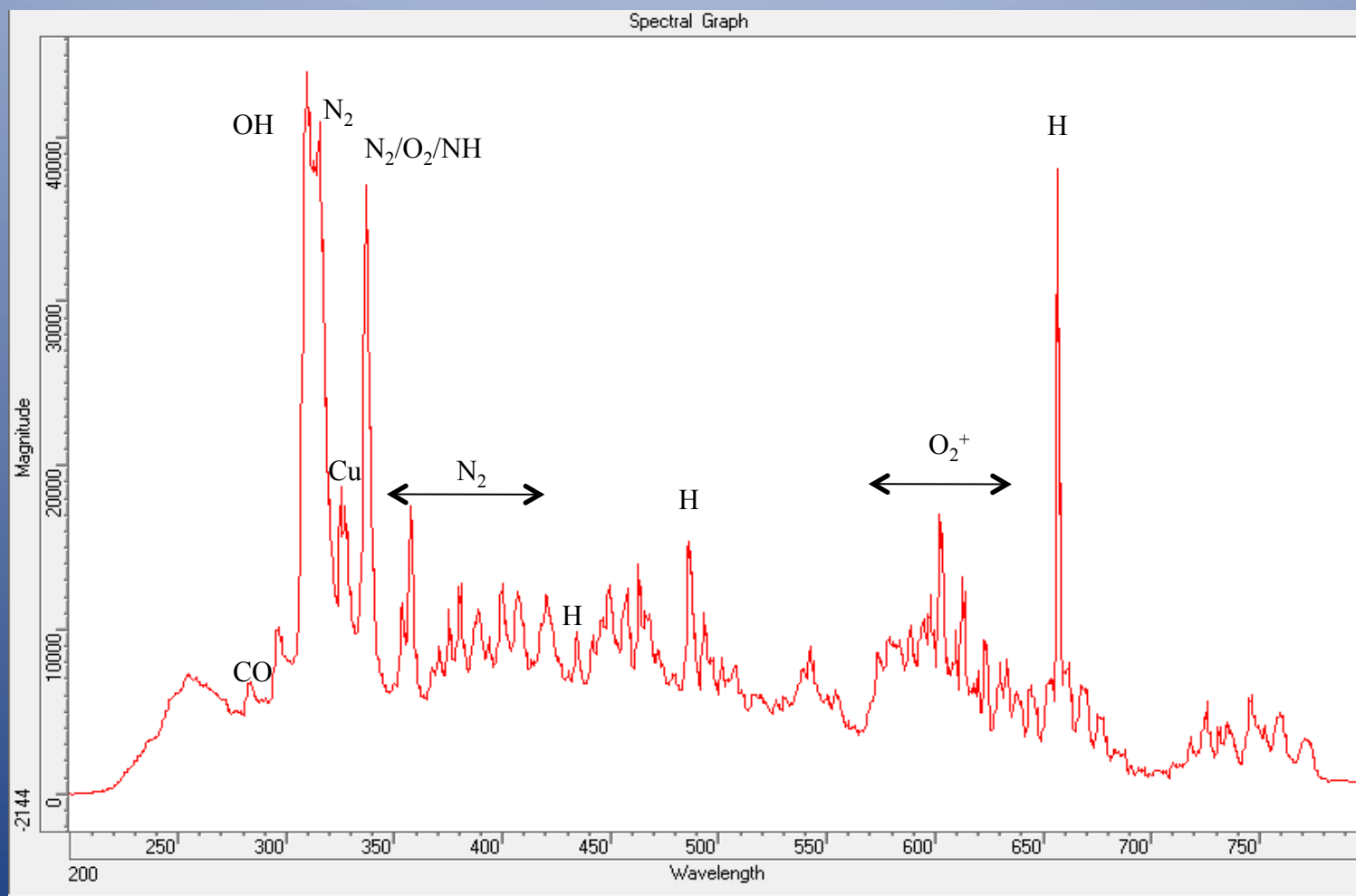
OES of H₂ Plasma



- Plasma Therm ICP reactor : 20 mtorr, 50 sccm H₂ , 10 °C

Effect of plasma contaminations

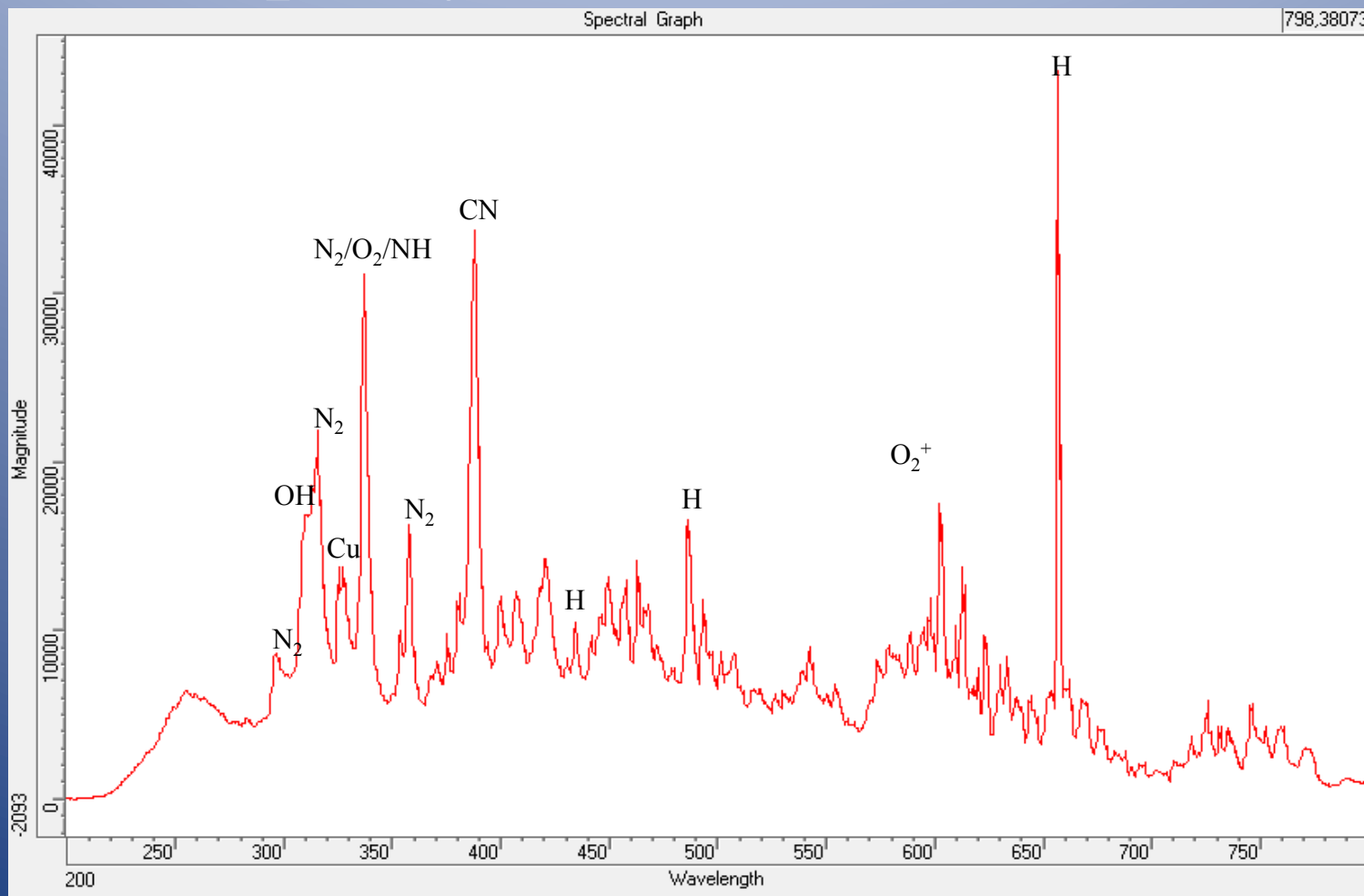
OES of H₂/O₂ Plasma



- Plasma Therm ICP reactor : 20 mtorr, 49 sccm H₂ + 1 sccm O₂, 10 °C

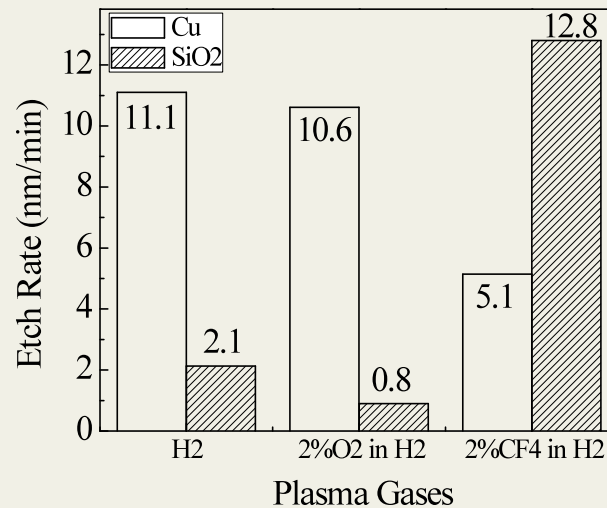
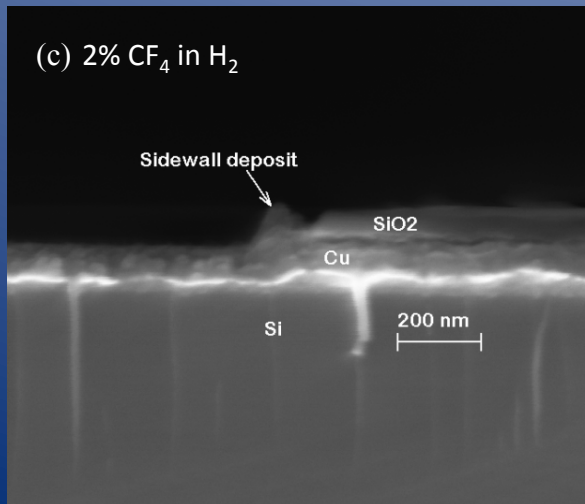
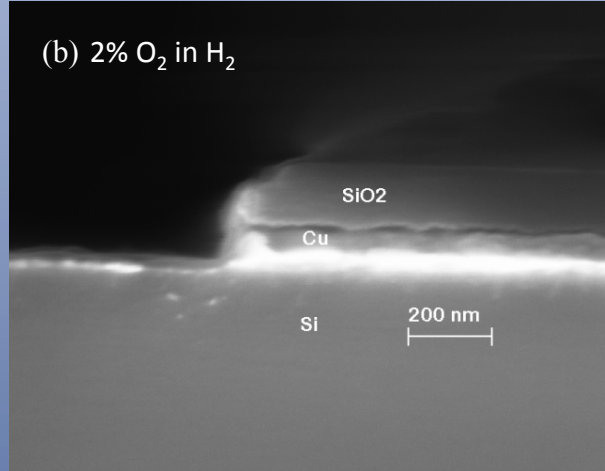
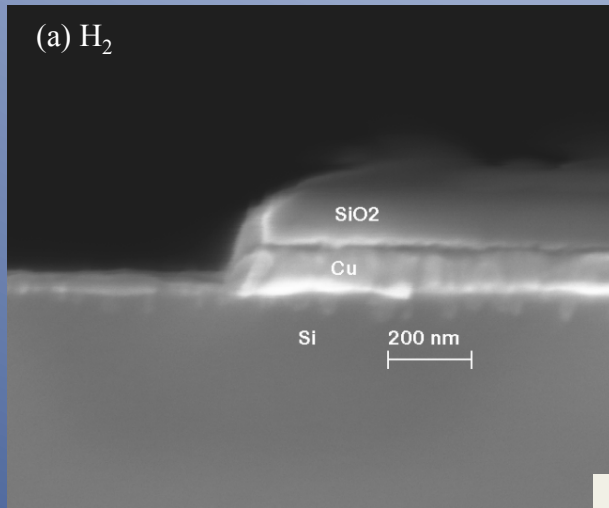
Effect of plasma contaminations

OES of H₂/CF₄ Plasma



- Plasma Therm ICP reactor : 20 mtorr, 49 sccm H₂ + 1 sccm O₂, 10 °C

Etch Rate Changes with Additives (O_2 or CF_4)



- Plasma Therm
ICP reactor : 20 mtorr, 10 °C
- H_2/O_2 : both ER ↓
- H_2/CF_4 :
 - Cu ER ↓ ↓
 - SiO₂ ER ↑ ↑
 - Sidewall deposition

Summary:

- Both chemical and physical components contribute to the hydrogen-based plasma etch of Cu;
- Mechanism may involve:
 - Chemical interactions of H with Cu
 - Ion bombardment
 - UV photon impingement
- Cu hydride is the possible etch product
- F, O, N, C contaminants demonstrated the robustness of the etch process

Acknowledgements

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